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AMMONIA REMOVAL FROM AGRICULTURAL RUNOFF AND SECONDARY EFFLUENTS BY SELECTED ION EXCHANGE

ADVANCED WASTE TREATMENT RESEARCH LABORATORY - V

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OHIO BASIN REGION
Cincinnati, Ohio

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AMMONIA REMOVAL FROM AGRICULTURAL RUNOFF AND SECONDARY EFFLUENTS BY SELECTED ION EXCHANGE

by

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for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

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U. S. Department of the Interior
Federal Water Pollution Control Administration
Cincinnati, Ohio

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FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity, and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research studies carried out under the guidance of the technical staff of the FWPCA Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

Reports in this series will be distributed as supplies permit. Requests should be sent to the Office of Information, Ohio Basin Region, Federal Water Pollution Control Administration, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

ABSTRACT

A selective ion exchange process was developed for the removal of ammonia nitrogen from wastewater. The process employs a natural zeolite, clinoptilolite, which is selective for ammonium ions in the presence of sodium, magnesium, and calcium ions. Regeneration of the exhausted clinoptilolite is accomplished with solutions or slurries containing lime. Lime provides hydroxyl ions which react with the ammonium ions to yield an alkaline aqueous ammonia solution. This ammonia solution is processed through an air stripping tower to remove the ammonia which is exhausted harmlessly to the atmosphere. The spent regenerant is then fortified with more lime and recycled to the zeolite bed to remove more ammonia. Since the regenerant is not discarded, the process generates no liquid wastes.

The ion exchange equilibria of four zeolites was investigated and clinoptilolite was selected for further study on the basis of its ammonium ion selectively and low cost. A cubic foot of granular clinoptilolite, regenerated with lime, was found capable of removing ammonia from more than 2000 gallons of secondary effluent. Ammonia removals exceeding 99% were obtained for two clinoptilolite columns in series during laboratory studies.

A mobile demonstration plant having a capacity of 100,000 gallons per day was designed and constructed to remove ammonia from wastewater. The plant contains facilities for flocculation, sedimentation, powdered activated carbon adsorption, disinfection, and mixed media filtration followed by ion exchange and associated regeneration equipment. Most of the equipment is housed in a forty foot trailer van which can be transported to different locations as needed. Other portable equipment includes, a 3500 gallon swimming pool which serves as a backwash water storage tank and ion exchange feed tank; two 500 gallon polyethylene regenerant storage tanks; and appropriate flexible rubber hose connections.

Operation of the mobile plant with secondary effluent resulted in ammonia removals of 97 and 93 percent at 70,000 and 100,000 gallons per day respectively; thus demonstrating that selective ion exchange provides a highly effective means for removing ammonia from wastewater.

RESEARCH REPORT

on

AMMONIA REMOVAL FROM AGRICULTURAL RUNOFF AND SECONDARY EFFLUENTS BY SELECTIVE ION EXCHANGE

to

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
WASHINGTON, D.C.

INTRODUCTION

The Need for Ammonia Removal

Early in the developing science of water pollution control, the presence of ammonia in surface and ground water supplies was regarded as a strong indication of recent pollution[1]. Klein[2] has stated that ammonia concentrations of greater than 0.2 mg/l are a strong indication of pollution by sewage. More explicitly, McKee and Wolf[3] state that: "The generally accepted limit for free ammonia for sanitary purity of water supplies is between 0.05 and 0.10 mg/l. Excess of this value renders the water suspect of recent pollution." While ammonia-nitrogen is commonly observed in surface waters it is not found in ground waters except in small amounts under anaerobic conditions[4].

As water quality science progressed, it became apparent that the presence of ammonia in water has far more serious implications than merely serving as an index of recent pollution. It was demonstrated that:

1) Ammonia can be toxic to fish and aquatic life.
2) Ammonia can contribute to explosive algae growths, thereby promoting eutrophication.
3) Ammonia can restrict wastewater renovation and water reuse.
4) Ammonia can have detrimental effects on disinfection of water supplies.
5) Ammonia can be corrosive to certain metals and materials of construction.

Where states have established water quality standards specifically for ammonia, it has been done primarily to protect the fisheries resources. Jones[5] pointed out that ammonia is one of the most important inorganic gases in regard to fish toxicity. Actually NH_3 is more toxic than the NH_4^+ ion. The ratio of NH_3 to NH_4^+ ion in an aqueous solution varies according to pH as shown in Figure 1[6]. Thus, toxicity is greatly dependent upon pH. The toxicity to fish is said to increase by 200 per cent or more between pH 7.4 and 8.0[3]. Likewise, toxicity increases as the dissolved oxygen concentration in water decreases, and as the hardness increases[5]. The presence of CO_2 can only reduce toxicity to a point where CO_2 then becomes a toxicant itself.

McKee and Wolf[3] have reported typical lethal ammonia exposures to fish. Some examples of these are: 0.3 to 0.4 mg/l for trout fry, and 0.7 to 5.0 mg/l for rainbow trout. They further state that the most widely used value for maximum recommended ammonia concentration is 2.5 mg/l in the pH range 7.4 to 8.5. The FWPCA National Technical Advisory Committee[7] has noted that other investigators have concluded that "... at pH levels of 8.0 and above total ammonia expressed as N should not exceed 1.5 mg/l."

The widely-publicized decline in Lake Erie water quality has focused national attention on the problem of accelerated eutrophication. One of the major manifestations of eutrophic conditions in lakes is the proliferation of algal blooms. These blooms result from excessive fertilization of the water body. Sawyer[8] has said that: "Ammonia nitrogen is the most important nitrogen stimulant to explosive algal growths (compared with nitrate nitrogen) and may be a factor in determining the type of bloom produced."

Ammonia can cause explosive algal growths due to the fact that it can be rapidly utilized by plant cells. Although nitrate can be stored in plant cells, it is only utilized following its reduction through the stages of nitrite and ammonia[9]. Dugdale and Dugdale[10] report that in the spring, in particular, ammonia nitrogen is more strongly assimilated by phytoplankton than any other nitrogen form.

Recent studies of future water demand have shown that unless water is used and reused judiciously the nation faces critical shortages in virtually all areas of the country by the year 2000. One potential solution to this

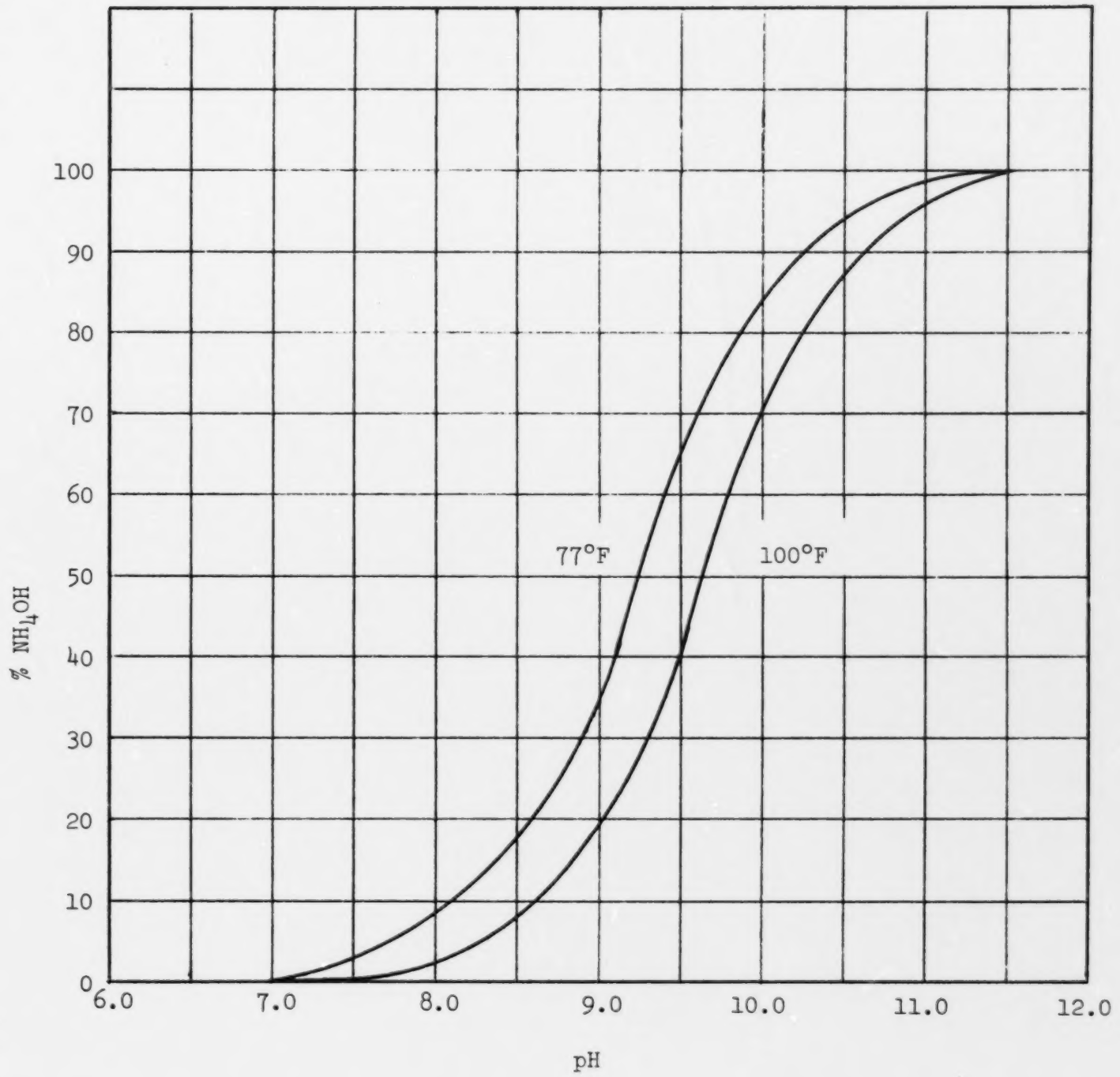

Figure 1. Percent NH_4OH in Water as a Function of pH.

problem is wastewater renovation and water reuse. The FWPCA has had a vigorous program in research and development in this area for some years. In summarizing this work Weinberger, et al.[11] had this to say: "In tests to date, long-term ion removal has been largely non-selective. The concentration of each ion present is reduced by roughly the same fraction. This is fortunate, because generally uniform removal is what is required to provide water of satisfactory quality for most purposes of reuse. One exception exists. Only a few parts per million of ammonia can be tolerated in municipal water supplies and in many industrial supplies. Since typical municipal waste water may contain 30 mg/l NH_4^+, the removal of 90-95 percent would be required. To achieve this by conventional electrodialysis would be prohibitively costly."

One reason why the need exists for ammonia removal from renovated water, and from public water supplies in general, is due to the fact that ammonia reacts with chlorine, the most commonly used disinfectant, to form chloramines. Mono- and dichloramine, while still bactericidal, are slower acting and less effective[12]. While the presence of ammonia during chlorination is not favored, it is frequently added in small amounts afterward to maintain a chlorine residual. As a matter of interest, Jones[5] reports that concentrations of chloramines as low as 0.4 mg/l are toxic to trout.

It is well-known that ammonia can be corrosive to certain metals and materials of construction, notably copper and zinc alloys[6][13]. In addition to being corrosive to copper and zinc, ammonium salts can also be destructive to concrete made from portland cement[3].

Sources of Ammonia in Wastewater

Potential sources of ammonia in wastewater which could cause concentrations requiring remedial action are shown in Table 1.

Table 1

Potential Sources of Ammonia in Wastewater

Agricultural Wastewater

- Animal feedlot drainage
- Overflows from livestock waste lagoons
- Irrigation return flows
- Drainage from land fertilized with animal manure
- Natural drainage from forested and agricultural land

Table 1 (Continued)

Municipal Wastewater

- Sewage
- Urban runoff

Industrial Wastewater (14)

- Basic chemicals
- Fertilizer
- Petroleum refining
- Steel rolling and finishing
- Coke and gas

The decomposition of nitrogenous organic matter represents the principal source of ammonia pollution.[3] In sewage[4] and in animal feedlot drainage, ammonia is a product of the hydrolysis of urea. Typical examples of ammonia concentrations encountered in sewage and animal feedlot drainage are 30 mg/l and up to 200 mg/l, respectively.

Concentrations of ammonia in irrigation return flows are generally less than 2.0 mg/l. Overflows from livestock waste lagoons produce variable concentrations of ammonia depending on lagoon design and loading factors. Sylvester[15] observed that urban street runoff has a much higher potential ammonia nitrogen content than forested or agricultural areas. He has reported some values as high as 7 mg/l as N for urban street drainage.

In the steel rolling and finishing industry[16] it has been stated that in 1963, the ammonia waste load was 8,660,000 pounds. The 1969 and 1977 waste loads are estimated to be 11,310,000 and 14,530,000 pounds, respectively. In steel mill coke oven gas, ammonium sulfate is produced by removing ammonia with sulfuric acid[16]. The major ammonia effluent streams in steel mill wastes are identified by Nemerow[17] as ammonia still wastes(187 mg/l as NH_3-N), and pure still wastes (10 mg/l as NH_3-N). Steam stripping is presently used for treatment of these effluents.

Fundamental petroleum refining processes which contribute major quantities of ammonia to process streams are crude oil distillation, catalytic cracking, and crude oil desalting[18]. Sour water contains the most significant amount of ammonia from these process streams, but some also appears in certain desalter effluent waters, phenolic condensates, and sour condensates[19].

In addition to the significant amounts of ammonia in sour water, high hydrogen sulfide concentrations are also evident. Steam stripping of sour water is normally carried out to remove sulfides; however, the removal of hydrogen sulfide requires an acidic pH, while ammonia removal occurs in the alkaline range. Hence, stripper effluent may contain from 100 to 2000 mg/l of ammonia depending on the influent ammonia concentration[18]. Because of the drastic effect of pH, ammonia removal efficiencies in sour water strippers can vary from 0 to 95 percent. Because of the amounts of ammonia in sour waters, by-product recovery is commonly practiced[19]. Steam stripping is also used to treat the desalter effluent waters, phenolic condensates, and sour condensates[19].

Air flotation, often used as one of the unit processes to treat the major refinery wastewater effluent, can be effective in stripping some ammonia if the pH is alkaline.

The coke and gas industry also produces waste streams containing ammonia[20]. Although the principal potential pollutant from the ammonia still is phenol, significant quantities of cyanide and ammonia are evident. The ammonia-containing effluent stream most likely to be directly discharged is the water layer from decanters following condensation. This stream contains from 5 to 30 mg/l of ammonia.

Stockyard wastes from meat packing contain 8 mg/l NH_3-N, and beet sugar wastes contain about 15 mg/l NH_3-N. Tannery effluents sometimes have NH_4Cl concentrations of 10 mg/l[17]. Other wastewaters streams in which ammonia might appear are those from ice plants, and from scouring and cleaning operation using "ammonia water"[3].

It is interesting to note that ammonia is added purposely to some wastewaters as a nutrient to aid in biological secondary treatment[21]. The pulp and paper and food processing industries commonly employ this practice.

Water Quality Standards - Ammonia

It has been shown in the previous discussion that considerable ammonia finds its way into environmental waters, and that ammonia can indeed cause degradation of water quality. Hence, it is no surprise that many standards have been promulgated to control the potential detrimental

effects of ammonia. Perhaps the standard of longest standing is the WHO European Drinking Water Standard. The recommended limit for ammonia is 0.5 mg/l as NH_4^+[3]. The Subcommittee for Public Water Supplies of the FWPCA National Technical Advisory Committee on Water Quality Criteria has suggested that the permissible ammonia criteria for water supplies should be 0.5 mg/l as N[7]. They further suggest that the desirable criteria should be less than 0.01 mg/l as N.

The Subcommittee for Fish, Other Aquatic Life, and Wildlife of the Advisory Committee has likewise made recommendations regarding desirable levels of ammonia[7]. Their recommendation for fresh water organisms is as follows: "Permissible concentrations of ammonia should be determined by the flow-through bioassay with the pH of the test solution maintained at 8.5, DO concentrations between 4 and 5 mg/l, and temperatures near the upper allowable levels." For marine and estuarine organisms the recommendation is: "Allowable concentrations of .... ammonia .... should be determined by the use of 96-hour TL_m values and appropriate application factors. Preferably, the TL_m values should be determined by flow-through bioassays in which environmental factors are maintained at levels under which these materials are most toxic. Tests should utilize the most sensitive life stages of species of ecological or economic importance in the area. Tentatively, it is suggested that application factors should be ... 1/20 for ammonia."

In their report to the State of California, Pomeroy and Orlob[4] state that for waters percolated to the ground the limit for ammonium ion should be less than 0.25 me/l average (4.5 mg/l as NH_4^+ or 3.5 mg/l as N).

In order to ascertain whether individual states have specifically designated ammonia standards in their water quality standards, all 50 states plus the District of Columbia, Guam, Puerto Rico, and the Virgin Islands were contacted*. As of the date of this writing (December 1, 1968), the following state water quality standards had not been approved by the Secretary of the Interior: California, Florida, Iowa, Kansas, Kentucky, Nebraska, Utah, Virginia, and Wyoming.

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*Copies of standards were not received from the following states: Arkansas, California, Connecticut, District of Columbia, Iowa, Kentucky, Missouri, New Jersey, Texas, and West Virginia.

Of the 44 standards received, only 13 had specific standards for ammonia. In most of the states which did not have ammonia standards, this substance can be included in those sections on "Toxic Substances" by implication. Generally, these states recommend that all toxic substances be excluded from surface waters at least in those concentrations which may be regarded as being detrimental to specified beneficial uses. Presumably, these detrimental effects will be determined by bioassay or observable effects. Delaware and Idaho have stated that they will use McKee and Wolf's Water Quality Criteria[3] as a guide in defining toxic substance concentrations.

Michigan, while not specifically designating an ammonia standard, made a general statement on nutrients, including phosphorus, ammonia, nitrates, and sugars. They state: "Nutrients originating from industrial, municipal or domestic animal sources shall be limited to the extent necessary to prevent adverse effects on water treatment processes or the stimulation of growths of algae, weeds, or slimes which are or may become injurious to the designated use."

Three of the states which were identified as having "ammonia standards" really have total nitrogen or nitrate standards. However, in two of the three cases the standards are so rigorous for these substances that it was believed reasonable to call attention to them. The states are Hawaii, Nevada, and South Dakota.

Hawaii - The total nitrogen content for the following classes of water shall not be exceeded: Class AA - 0.10 mg/l, Class A - 0.15 mg/l, and Class B - 0.20 mg/l.

Nevada - The value for nitrates shall be not more than 1.0 to 7.0 mg/l depending upon the designated water course. In Lake Tahoe, the annual average total soluble inorganic nitrogen concentration shall not exceed 0.025 mg/l.

South Dakota - For domestic water supply the nitrate concentration shall not exceed 10 mg/l as N, or 45 mg/l as NO_3^-. For wildlife propagation and stock watering the nitrate concentration shall not exceed 50 mg/l as NO_3^-.

The specific ammonia standards for the remaining 10 states will be described below.

Arizona - For those waters designated for the propagation of aquatic and wildlife resources ammonia concentrations shall not exceed 1.5 mg/l.

Guam - For public or domestic water supply ammonia nitrogen shall be less than 0.01 mg/l as N.

Illinois - In general, ammonia nitrogen concentrations shall be less than 2.5 mg/l; however, for various waters of the state more stringent values will be imposed. Specific examples are: Little Calumet River - 1.5 mg/l (single daily value); Lake Michigan open water - 0.02 mg/l (annual average) and 0.05 mg/l (single daily value); and Lake Michigan shore water - 0.05 mg/l (annual average) and 0.12 mg/l (single daily value).

Indiana - Indiana's ammonia standards are almost identical to Illinois as might be expected. For example, in Lake Michigan open and shore water, and in the Little Calumet River the values are exactly the same. An additional example is the standard for ammonia in the Indiana Harbor Canal (the control point is the Indiana Harbor Breakwater Inner Light) - 1.0 mg/l for the annual average, and 1.5 mg/l for a single daily value.

Massachusetts - Class B - ammonia shall not exceed an average of 0.5 mg/l as N during any monthly sampling period. Class C - not to exceed 1.0 mg/l as N. Classes SA and SB - not to exceed 0.2 mg/l as N. Class SC - not to exceed 1.0 mg/l as N.

Minnesota - Fisheries and recreation-ammonia concentrations shall be less than the following values for these categories of use: cold water fishery and/or whole body contact - trace; mixed fishery and/or whole body contact - 1.0 mg/l; and resident fish and/or partial body contact - 2.0 mg/l.

Nebraska - The draft of Nebraska's water quality standards included the following statement and the accompanying table (Table 2). "Ammonia nitrogen concentrations shall not exceed 1.4 mg/l in trout

TABLE 2

MAXIMUM PERMISSIBLE LIMIT OF AMMONIA EXPRESSED AS N
AT VARIOUS pH VALUES

pH	Maximum Limit of Ammonia Expressed as parts per million N	
	Trout Waters	Warm Waters
8.3	1.4	3.5
8.4	1.2	2.9
8.5	1.0	2.4
8.6	0.84	2.1
8.7	0.72	1.8
8.8	0.60	1.4
8.9	0.56	1.2
9.0	0.48	1.1

streams nor exceed 3.5 mg/l in warm water streams where the pH in these streams does not exceed a pH value of 8.3. If the pH of a stream exceeds 8.3, the undissociated ammonium hydroxide as nitrogen shall not exceed 0.1 mg/l in trout streams nor exceed 0.25 mg/l in warm water streams."

New York - The appropriate standard for New York is quoted as follows: "With reference to certain toxic substances as affecting fish life, the establishment of any single numerical standard for waters of New York State would be too restrictive. There are many waters, which because of poor buffering capacity and composition will require special study to determine safe concentrations of toxic substances. However, based on non-trout waters of approximately median alkalinity (80 ppm) or above for the State, in which most of the waters near industrial areas in this State will fall, and without considering increased or decreased toxicity from possible combinations, the following may be considered as safe stream concentrations for certain substances to comply with the above standard for this type of water. Waters of lower alkalinity must be specially considered since the toxic effect of most pollutants will be greatly increased .... Ammonia or ammonium compounds -- not greater than 2.0 ppm (NH_3) at pH of 8.0 or above."

North Dakota - For portions of the Red River and other designated and related waters the ammonia concentration shall not exceed 2.0 mg/l.

Puerto Rico - For surface waters: "The concentration of ammonia shall not be increased by more than 0.02 mg/l as a monthly average. Maximum permissible concentrations for a single sample is 3 times the established limit, provided this limit must not be exceeded in more than 5% of such samples."

Remedies - Ammonia Removal from Wastewater

Just as the detrimental effects of excessive ammonia concentrations in water have been studied for many years, so have potential remedies. Rohlich[22] summarized some of the methods which have been investigated. He has reported that the Guggenheim process of the 1930's used a zeolite for ammonia removal. Presumably this zeolite was greensand or glauconite. It was quite effective in reducing initial concentrations of ammonia of 12 to 14 mg/l to an effluent concentration of 0.5 to 1.0 mg/l.

Rohlich[22] also reported on the work of Nesselson who used nuclear sulfonic cation exchangers for ammonia as well as other pollutants. Despite the apparent success of this method, the nonselective nature of conventional ion exchangers makes the cost of this process prohibitive. In addition, if conventional ion exchange were used for ammonia removal, excessive regenerant wastes would be encountered.

Air stripping of ammonia was also discussed by Rohlich[22]. However, even though removals of 92 percent were reported, it was believed that the economics of the process were unfavorable. On the other hand, more recent experience with air stripping has resulted in more explicit data[23]. Using a recommended value of 1 mg/l for ammonia, research on air stripping has shown the cost of the process to be about 2¢/1000 gal: not including the cost of lime and solids removal from product water. The lime cost to raise wastewater pH to 9.9 was determined to be about 3¢/1000 gal. A cost saving would result if lime recovery was practiced. The FWPCA has concluded that air stripping can be applied most conveniently in combination with lime treatment.

Steam stripping has been employed widely in the petroleum refining industry for ammonia removal, but for the lower concentrations encountered in most ammonia-laden streams it is quite costly.

Other processes have been unsuccessful in removing appreciable amounts of ammonia. Malhotra et al.[24] showed that there is no ammonia removal during alum precipitation. Likewise, electrodialysis, because of its non-selectivity, cannot be effectively employed for ammonia removal[11]. Similar findings have been reported for reverse osmosis.

In summary, it would appear that a selective method for removing the ammonium ion from wastewater would be highly effective and economical when compared with other nonselective methods such as conventional ion exchange, electrodialysis, and reverse osmosis. Furthermore, steam and air stripping are rate limited at lower ammonia concentrations and as a result, it is very costly to achieve effluent concentrations of about 1 mg/l, a commonly recommended value. Even in distillation, ammonia appears in the condensate. The selective ion exchange method for removing ammonia from wastewater reported here demonstrates exceptional promise for solving one of the nation's water pollution problems. In addition, the information attained on selective ion exchange in this study can prove to be helpful when applied to other problems in water pollution control.

Conclusions and Recommendations

The removal of ammonia from secondary effluent was successfully demonstrated on a laboratory and pilot scale using a selective ion exchange process. The significant results of this program are:

(1) Greater than 99% ammonia removal was demonstrated in the laboratory with two zeolite columns in series and clarified secondary effluent containing 10 to 19 mg/l ammonia nitrogen. From 200 to 300 column volumes of secondary effluent can normally be processed to full column loading.

(2) Laboratory elution studies show that regeneration can be accomplished with about 20 column volumes of recycled regenerant containing lime applied at the rate of 10 column volumes per hour. More than 95% of the available ammonia capacity was restored with this treatment. The presence of sodium ion in the recycled regenerant minimizes the volume of regenerant required for elution of the ammonia.

(3) No liquid regenerant waste is produced since the spent regenerant is air stripped to remove ammonia and reused after the addition of more lime. The ammonia is exhausted harmlessly to the atmosphere from the air stripper.

(4) Residual alkalinity in a freshly regenerated clinoptilolite bed causes some ammonia leakage during the initial part of the loading cycle. Backwashing with ammonia free water (i.e. product water from the clinoptilolite beds in service) is recommended for removing the residual alkalinity.

(5) An average ammonia removal of 97% was attained for two 500 gallon clinoptilolite columns in the mobile demonstration plant with clarified secondary effluent containing 16 mg/l ammonia nitrogen. The flow rate was 6.0 gal/ft^2/min for a total of 70,000 gallons per day.

(6) An average ammonia removal of 93% was attained for two 330 gallon clinoptilolite columns with secondary effluent containing 15 mg/l ammonia nitrogen. Although the secondary effluent was simply filtered through a multimedia filter without chemical coagulation, no zeolite bed plugging problems were encountered with this feed. The flow rate was 8.4 gal/ft^2/min for a total of 100,000 gallons per day. Laboratory studies indicated fouling of the zeolite with unclarified secondary effluent.

(7) Elution of ammonia from the mobile demonstration ion exchange columns with recycled regenerant was quite effective; however, regeneration time was longer than anticipated due to low stripping efficiency. Optimum air-liquid contact was apparently not attained in the air stripping tower.

Although the number of pilot scale studies were limited due to expiration of the contract, the selective ion exchange process shows great promise as an effective, economical method for removing ammonia from wastewater. Further pilot scale studies are recommended with the mobile demonstration plant following minor alterations to improve the regeneration system. Areas requiring further study include: (1) accurate determination of clinoptilolite attrition through extended operation of the mobile demonstration plant, (2) effect of temperature (climate) and (3) effect of wastewater composition (i.e. high salt vs low salt).

LABORATORY STUDIES

Zeolite Ion Exchange Equilibria

The ion exchange equilibria of four zeolites were investigated to determine their selectivity for ammonium ion in the presence of other cations normally found in relative abundance in most wastewaters. These zeolites were chosen on the basis of their high cesium ion selectivity[25].

The natural clinoptilolite used in this study was from the Hector, California area. The occurrence of the Hector clinoptilolite deposit has been described elsewhere[26]. The AW 400 and AW 500 are zeolites produced by the Linde Company*, and Zeolon® is a product of the Norton Company.** The properties of these zeolites are listed in Table 3.

TABLE 3

ZEOLITE PROPERTIES

Zeolite	SiO_2/Al_2O_3	WT % Binder	Wt % H_2O, 25°C	Structural Type	NH_4^+ Capacity, meq/g
AW 500	4-5	25	15	Chabazite	1.67
AW 400	6-7	25	12	Erionite	1.88
Zeolon	10	--	12	Mordenite	2.02
Hector Clinoptilolite	8-10	5-20	12	Clinoptilolite	1.81

All of the capacities given in Table 3 are for the zeolite with the amounts of binder and water indicated. Capacities measured with cations other than ammonium can be substantially different.

Equilibrium studies were accomplished by utilizing a small column technique similar to that reported by Howery and Thomas[27]. One-half gram of 30 to 50 mesh zeolite was placed in a straight sealing tube containing a fritted glass disc. The sealing tubes had been cut off just below the frit to allow placement of the tube and zeolite into a 500 ml Kjeldahl flask for ammonia determination. A solution of known chemical composition was slowly passed through the zeolite column until equilibrium was attained. The contact time and solution volume necessary to reach equilibrium was determined previously by passing several volumes of influent through a group of columns and

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* Linde Company - Tonawanda, New York

** Norton Company - Worchester, Massachusetts

ascertaining the volume and time elapsed before ammonium ion values on the zeolite remained constant. By obtaining several equilibrium points with constant normality influents of variable cation ratio, an isotherm could be determined for each binary system. The isotherm represents a series of equilibrium points at the same temperature between the equivalent fraction of one of the cations on the zeolite and the equivalent fraction of the same cation in the equilibrium solution.

From the solution and zeolite cation compositions, a selectivity coefficient, K_A^B , was obtained with the following relationship:

$$K_A^B = \frac{(A)_z^{nA} \quad (B_N)^{nB}}{(B)_z^{nB} \quad (A_N)^{nA}},$$

where (A_N) , (B_N) = normality of cations A and B in the equilibrium solution,
$(A)_z$, $(B)_z$ = equivalent fractions of cations A and B on the zeolite, and
nA, nB = the number of moles of A and B represented in the chemical equation for the exchange reaction of A and B.

In conjunction with ammonium ion removal, the main competing cations in natural waters normally will be sodium, calcium, magnesium and potassium. The present study, therefore, is concerned with zeolite ammonium selectivities from the binary systems sodium-ammonium, calcium-ammonium, magnesium-ammonium, and potassium-ammonium.

The use of organic cation exchange resins for selective ammonium ion removal from systems containing divalent cations did not prove to be feasible. A comparison of Hector Clinoptilolite and a strong acid polystyrene resin, IR 120, is shown in Figure 2. A diagonal drawn from zero ammonium ion on the resin and in solution to 1.0 ammonium ion on the resin and in solution is a straight line representing no cation selectivity. Any isotherm below the no selectivity line represents an isotherm with ammonium selectivity values of less than 1.0, in which case the exchanger is selective for calcium. If the isotherm is above the diagonal line, the exchanger is selective for the cation being measured, or ammonium ions. The IR 120 prefers calcium to ammonium ions, as Figure 2 shows. The Hector Clinotilolite,on the other hand, prefers ammonium to calcium ion, and hence would be of greater utility for ammonium ion removal from calcium systems. Other organic resins were studied and gave similar results.

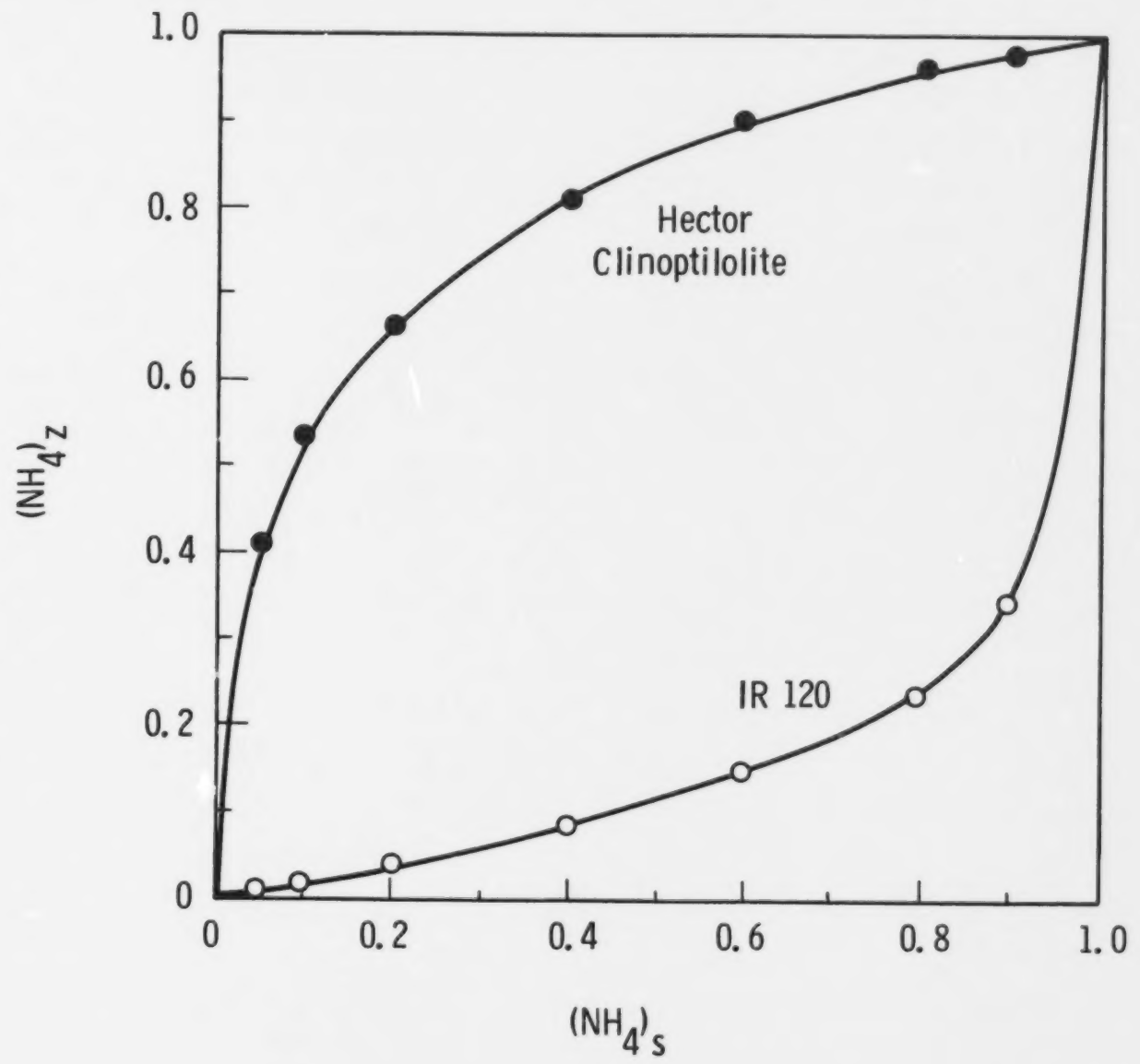

Figure 2. The 23°C isotherms for the reaction, $(Ca)_z + 2(NH_{4_N}) = 2(NH_4)_z + (Ca_N)$ with Hector clinoptilolite and IR 120. Total equilibrium solution normality was constant at 0.1N$(Ca)_z$, $(NH_4)_z$ = equivalent fraction of calcium or ammonium on the zeolite. (Ca_N), (NH_{4_N}) = normality of calcium or ammonium in the equilibrium solution. The ammonium capacity of IR 120 was 4.29 meq/g of air-dried resin.

Isotherms for the systems sodium-ammonium, calcium-ammonium, magnesium-ammonium and potassium-ammonium with the zeolites AW 500, AW 400, Zeolon and Hector Clinoptilolite were determined at 23°C[28]. Two general characteristics of the isotherms were noted. The first characteristic is that all of the above zeolites prefer potassium to ammonium ions, and the second that all are ammonium-selective in systems containing calcium, sodium and magnesium.

Selectivity coefficients may be determined at several points on the isotherm, and these values plotted vs. corresponding ratios of cation normalities in the equilibrium solution. The results of such a plot are presented for magnesium-ammonium, calcium-ammonium, sodium-ammonium and potassium-ammonium with Hector Clinoptilolite in Figures 3 and 4, respectively. It may be noted that Hector Clinoptilolite has a much greater preference for NH_4^+ over Mg^{+2} and Ca^{+2} in strong salt solutions of these ions. This preference or selectivity diminishes somewhat due to the mass action effect in dilute salt solution. The above plots are useful for estimating zeolite ammonium ion loadings for different waste compositions.[28]

Small Column Studies

Clinoptilolite was chosen for further study in column experiments on the basis of good ammonium ion selectivity combined with potential low cost. Clinoptilolite is available in several large natural deposits in the Western United States. The small column experiments were conducted with 1.9 cm diameter by 12.34 cm high beds of either 20 x 50 mesh or 50 x 80 mesh clinoptilolite to obtain an estimation of the relationship between flow rate, effluent ammonium content, and grain size range prior to setting up larger columns. The results indicated that somewhere between 20 and 30 column volumes/hr, the 20 to 50 mesh size range exhibited poor exchange kinetics with a simulated secondary effluent.[28] The slope of the ammonium breakthrough curve became relatively shallow, and leakage of ammonium occurred early in the loading cycle.

Improved kinetics were apparent with use of the 50 x 80 mesh clinoptilolite grain size because the slope of the breakthrough curve did not change appreciably until flow rates greater than 40 column volumes/hr were attained.

A clinoptilolite grain size range of 20 to 80 mesh would probably allow column flow rates of 30 to 35 column volumes/hr for ammonium loading. The

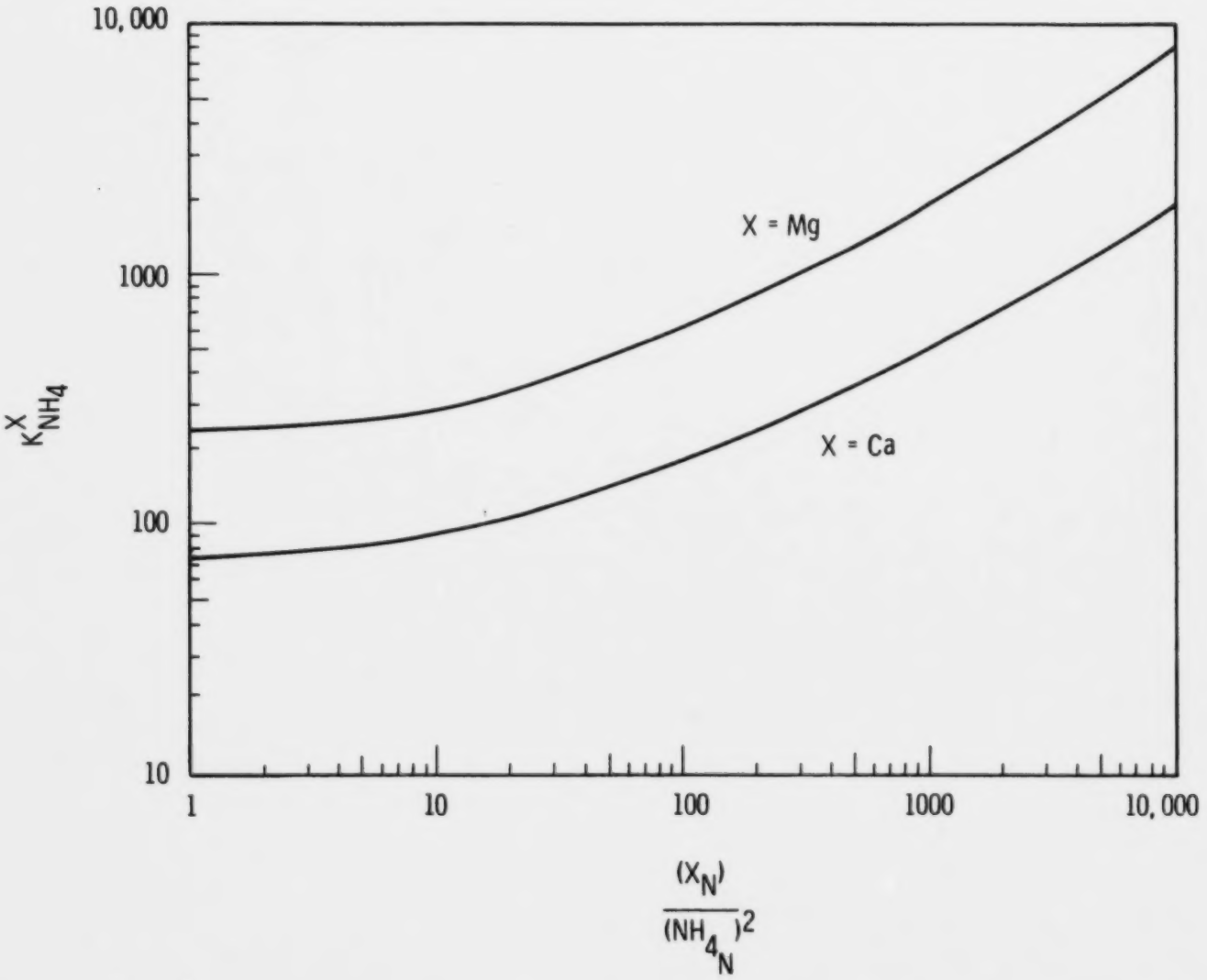

Figure 3. Selectivity coefficients vs. concentration ratios of calcium or magnesium and ammonium in the equilibrium solution with Hector clinoptilolite at 23°C for the reaction $(X)_z + 2(NH_4)_N = 2(NH_4)_z + (X)_N$

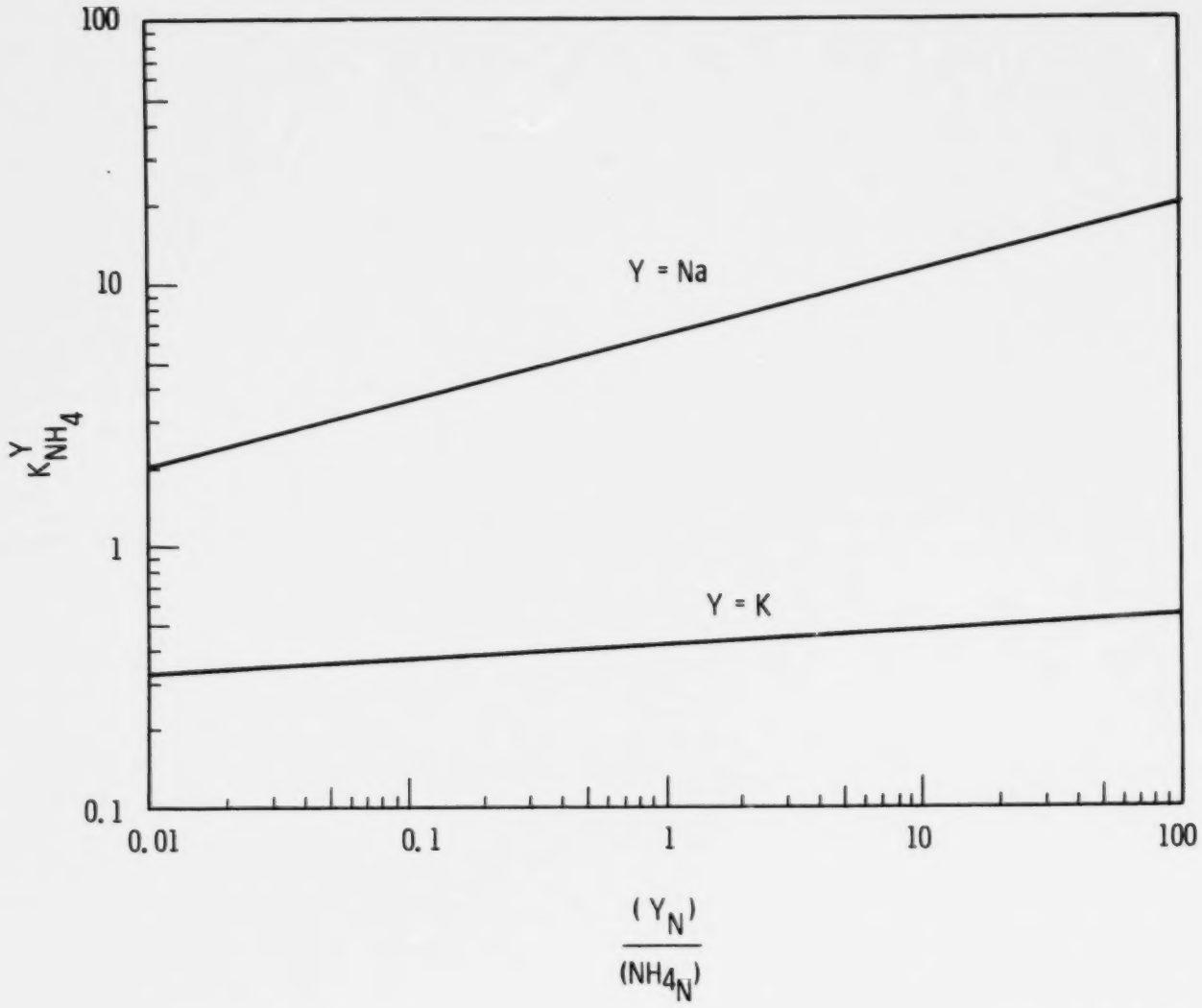

Figure 4. Selectivity coefficients vs. concentration ratios of sodium or potassium and ammonium in the equilibrium solution with Hector clinoptilolite at 23°C for the reaction $(Y)_z + (NH_4)_N = (NH_4)_z + (Y)_N$

column could either be loaded downflow to avoid fluidizing the bed, or be mechanically restrained for upflow loading. However a potential disadvantage of small grain sizes is the high head loss often experienced in their use.

The effect of temperature on the ammonium elution rate was determined for 20 to 50 mesh Hector clinoptilolite column loaded with an equilibrium mixture of $1.2\underline{N}$ NH_4Cl + $0.83\underline{N}$ KCl.[28] The elution samples were collected in an acidic solution, transferred to a Kjeldahl apparatus and made basic in pH. The ammonia from the boiling sample was collected in boric acid and titrated with a standard acid to the original boric acid pH. Partial elution curves were determined with a slurry containing 4.5 g/l of $Ca(OH)_2$ at 0°C, 10°C, 45°C and 80°C, along with a complete elution curve at 23°C. Zero degrees and 80°C represented the slowest elution rates, requiring 80 to 120 column volumes to 100 percent elution. The 10°C and 45°C elution rates were intermediate, and the 23°C curve required 34 to 40 column volumes of a $Ca(OH)_2$ slurry for 100 percent elution. The 23°C elution rate probably represented an optimum between $Ca(OH)_2$ solubility in the eluting solution and cation exchange kinetics. A relatively high temperature resulted in favorable exchange kinetics but low $Ca(OH)_2$ solubility, while a low temperature yielded high $Ca(OH)_2$ solubility but poor exchange kinetics.

Elution with a solution containing $0.1\underline{N}$ NaCl + 5g/l of $Ca(OH)_2$ was tried at 23°C and 45°C. The added NaCl minimized the $Ca(OH)_2$ temperature effect and speeded ammonium elution, and thereby represented an improvement over elution with $Ca(OH)_2$ slurry alone.

At 25 column volumes, the $Ca(OH)_2$ slurry alone had eluted 90 percent of the ammonium on the column while the NaCl-$Ca(OH)_2$ solution had eluted 90 percent of the ammonium, at 16 column volumes.

After some calculations on the respective pH of the equilibrium solutions of $Ca(OH)_2$ and $Mg(OH)_2$, it became apparent that precipitation of the magnesium eluted from the column with a $Ca(OH)_2$ slurry would occur. Consequently, comparative $Ca(OH)_2$ slurry elution studies were made between clinoptilolite columns loaded with the ammonium with and without magnesium. At 40 column volumes, the percentage of ammonium eluted was 98 for the two columns with magnesium and 99.3 for the column without magnesium. The presence of magnesium on the column has little or no effect on the ammonium elution rate. Likewise, little grain size range effect was shown between 20 to 50 and 50 to 80 mesh clinoptilolite columns loaded with ammonium and magnesium solution.

Although a $Ca(OH)_2$ slurry was used during the elution studies, the flow rate was held to seven column volumes/hr. The clinoptilolite bed was not raised at that flow rate, so the $Ca(OH)_2$ slurry only partially penetrated the clinoptilolite bed. In effect, therefore, the elution data were obtained with a saturated solution of $Ca(OH)_2$ rather than an excess $Ca(OH)_2$ slurry. The small diameter columns were not suitable for fluidized bed studies. It will be necessary, however, to fluidize the bed after elution with $Ca(OH)_2$ slurry to remove the $Ca(OH)_2$-$Mg(OH)_2$ solids. We may conclude that saturated $Ca(OH)_2$ solution (1.7 g/l at 23° or 0.023$\underline{M}$) sufficed to remove the ammonium from the clinoptilolite.

Characterization of Secondary Effluent

Periodic grab samples of secondary effluent were taken for chemical analysis from the No. 2 chlorinator basin at the Richland, Washington, Wastewater Treatment Plant during the spring, summer, and fall months of 1967. This effluent stream was used for both laboratory and pilot plant studies. The average characteristics of the secondary effluent are listed in Table 4. Since the cation concentrations including ammonium ion are of particular importance to the ion exchange process the concentration variation over the nine month period covered is illustrated in figures 5 and 6.

The Richland Wastewater Treatment Plant is a normal high rate trickling filter operation. Since the treatment plant receives essentially no industrial wastes, the flow of approximately 3 million gallons per day is almost entirely of domestic origin.

Table 4

Average Characteristics of Richland Secondary Effluent

Ammonia as nitrogen	15 mg/l
Sodium	58 mg/l
Potassium	12 mg/l
Magnesium	8 mg/l
Calcium	34 mg/l
Alkalinity as $CaCO_3$	180 mg/l
Ortho phosphate as phosphorus	9 mg/l
Sulfate as sulfur	20 mg/l
Nitrate as nitrogen	1 mg/l
COD	83 mg/l
pH	7.3
Specific conductance	630 mhos/cm

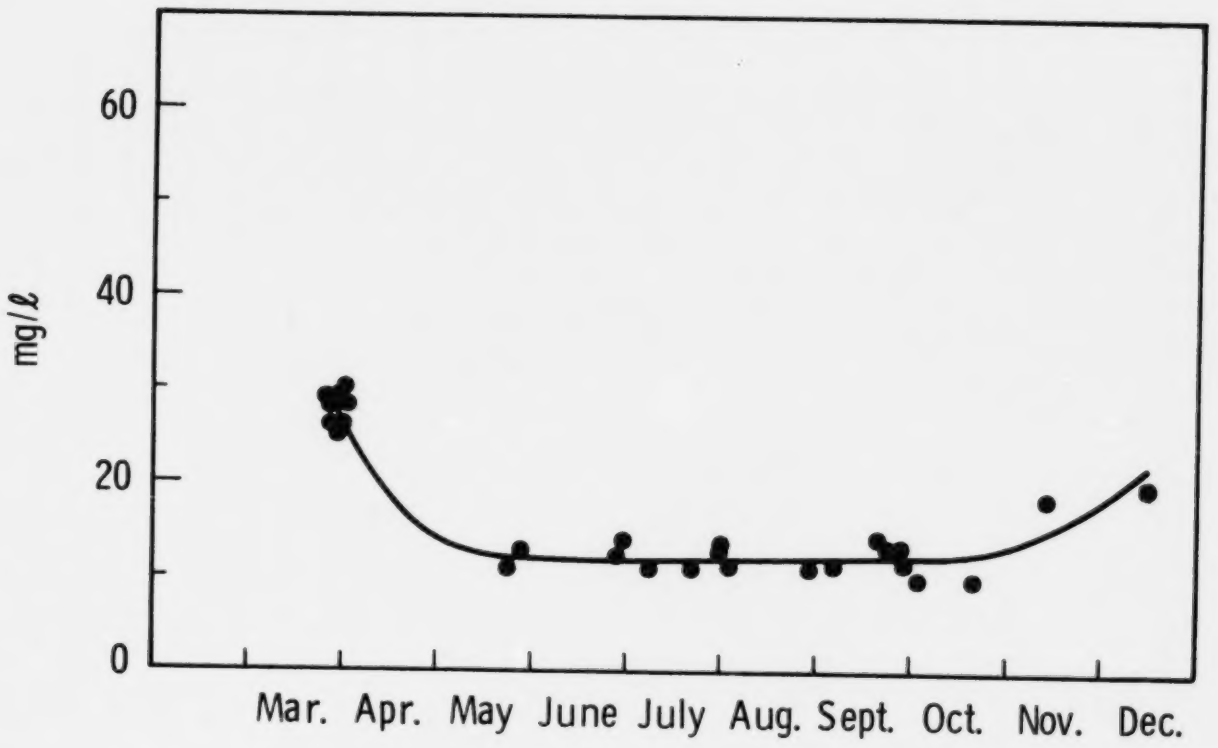

Figure 5. Ammonia Nitrogen Concentrations in Richland Secondary Effluent

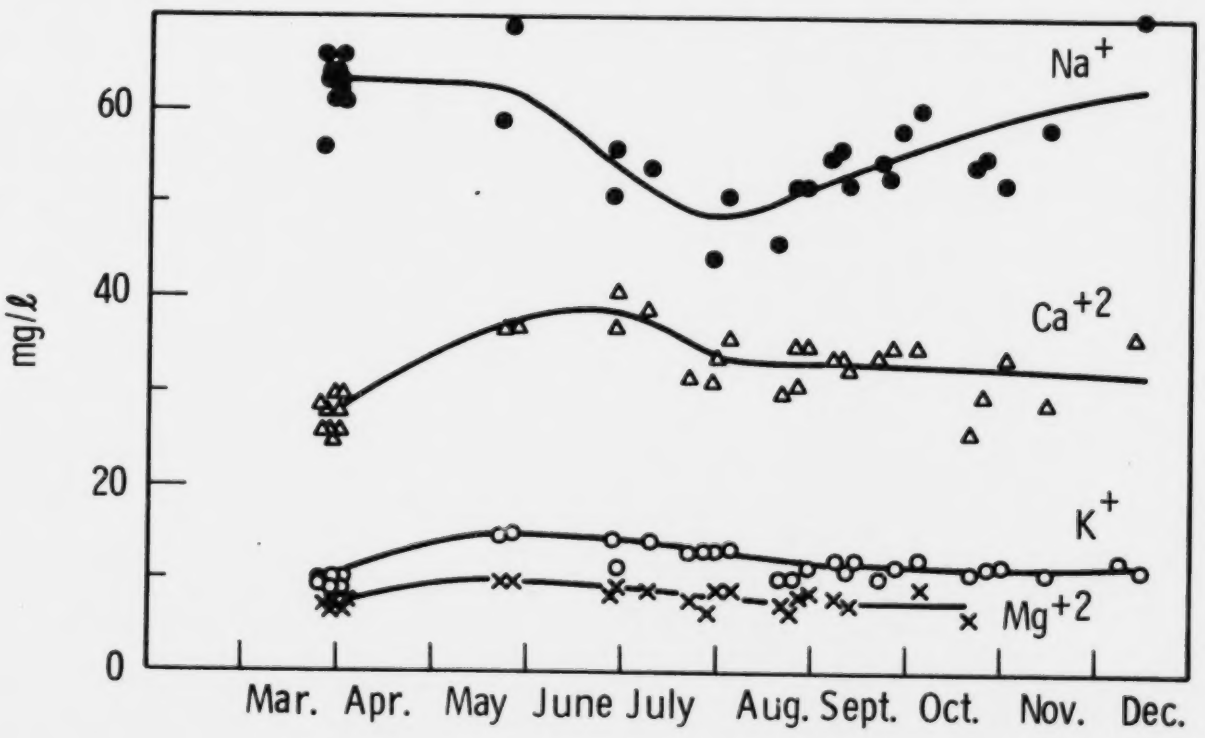

Figure 6. Metal Cation Concentrations in Richland Secondary Effluent

Two Inch Column Studies

Laboratory experiments were conducted with 2 inch diameter by 24 inch columns of granular clinoptilolite to provide scale-up data for the mobile pilot plant design. The flow sheet used for most of the laboratory runs is shown in Figure 7. A second clinoptilolite column was added during the final phase of the laboratory work to evaluate the performance of two clinoptilolite columns in series.

The clinoptilolite beds were contained in thick wall glass pipe 2 inches inside diameter by 36 inches in length. Feed solutions were pumped to the clinoptilolite beds with a centrifugal pump while the feed flow rate was regulated by means of a pneumatically operated valve. Regenerant solutions or slurries were pumped through the beds with a separate centrifugal pump.

The removal of ammonia from untreated Richland secondary effluent was investigated since it may be desirable in some cases to remove the ammonia without removing suspended solids. The column was operated upflow to prevent plugging of the clinoptilolite beds. The removal of ammonia in this manner is illustrated in Figure 8, along with regeneration of the bed with a lime slurry, at a loading rate of 16.6 cv/hr. (column volumes/hour). The 20 x 50 mesh clinoptilolite was expanded to about 125% of the settled volume during loading. Little fluidization occurred at this flow rate; however, channeling was observed throughout the bed resulting in some loss in ammonia removal efficiency. Subsequent examination of the clinoptilolite indicated that organic fouling reduced the available ion exchange capacity by about 25% during two upflow runs with untreated secondary effluent. The capacity was regained by heating the clinoptilolite to 400°C for 2 hours in a muffle furnace.

The remaining 2 inch column experiments were conducted with pretreated Richland secondary effluent. Pretreatment of the secondary effluent from the Richland Wastewater treatment plant included: (1) lime coagulation without activated carbon adsorption, (2) lime coagulation with carbon adsorption, and (3) alum coagulation with carbon adsorption. The flow sheet given in Figure 7 illustrates pretreatment (2). The secondary effluent was treated with 200-300 mg of $Ca(OH)_2$ per liter to coagulate suspended matter. After sedimentation in a 200 gallon polyethylene tank, the supernatant liquid was decanted to a second 200 gallon polyethylene tank. The liquid was

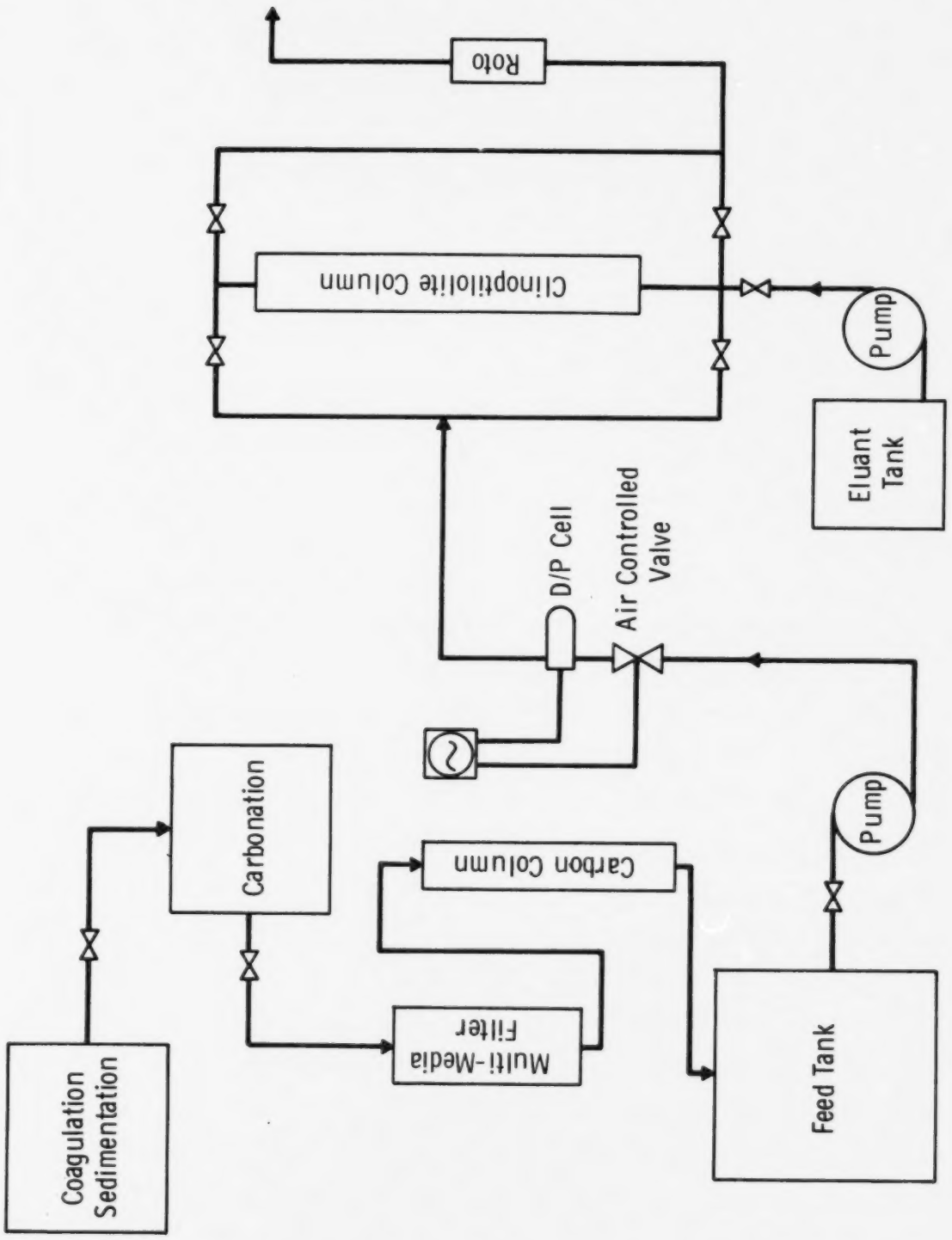

Figure 7. Flow Sheet for Single 2-Inch Column Runs

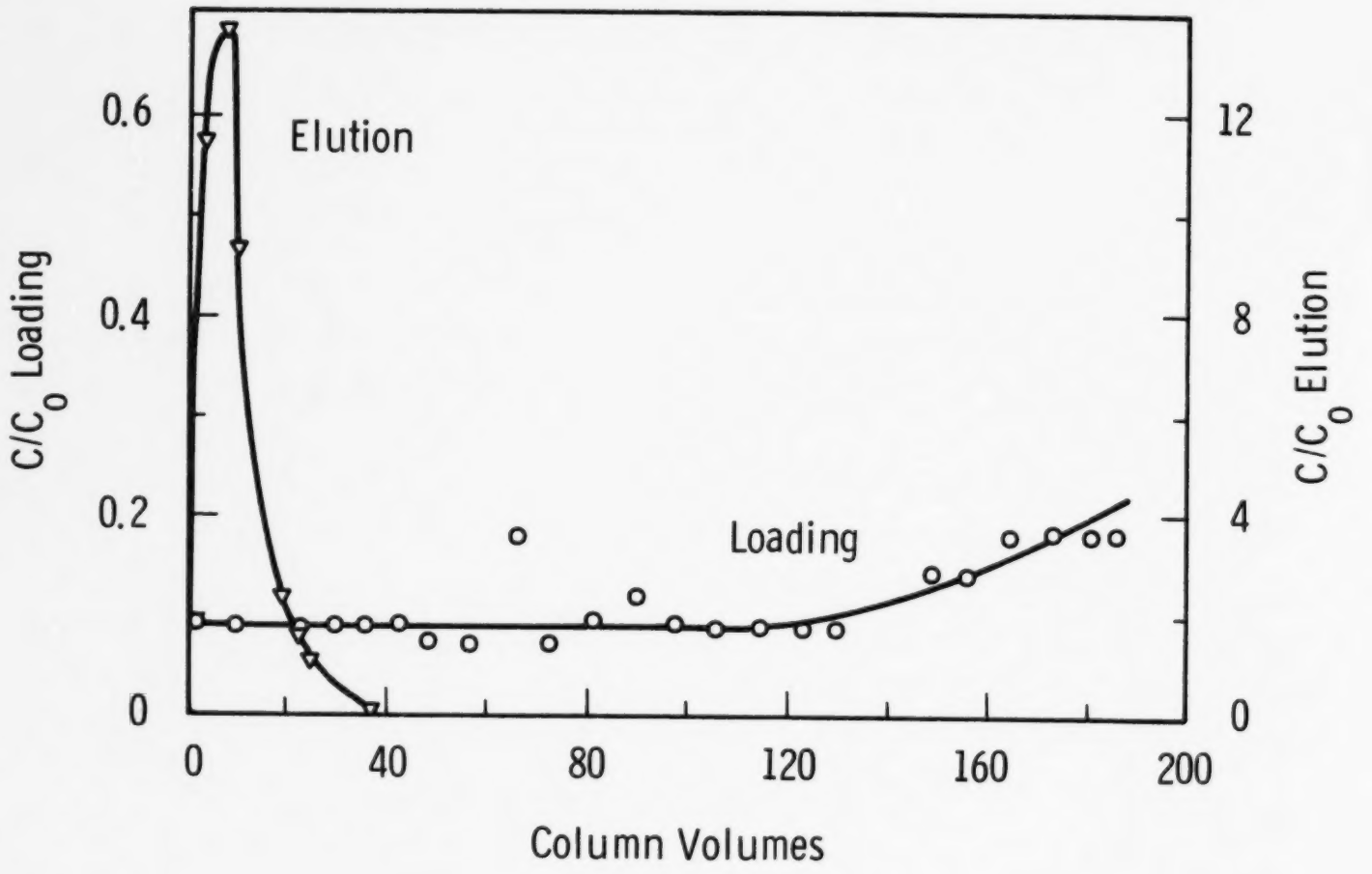

Figure 8

Loading and Elution Curves for Upflow Operation
with Untreated Richland Secondary Effluent

Loading Flow Rate	16.6 cv/hr
Column Dimensions	2" diameter by 24" depth (settled)
Clinoptilolite grain size	20 x 50 mesh
Temperature	28°C
Elution flow rate	10.3 cv/hr
Eluant	4.5 g/l $Ca(OH)_2$ slurry
Influent NH_4^+	10.9 mg/l as NH_3 - N
Feed	Untreated Richland secondary effluent

sparged with CO_2 to pH 9.4 to reduce the Ca^{+2} concentration by precipitation of $CaCO_3$. Polyelectrolyte*(8 mg/l) was added to aid sedimentation and filtration. The mixture was then passed through an anthracite-sand filter and a column of granular activated carbon to remove suspended matter and dissolved organic matter. The filtrate flowed to a 500 gallon polyethylene feed tank where the pH was adjusted to about 6.5 prior to pumping through the zeolite column. The clarity of the filtrate after carbonation was excellent in all runs. No clinoptilolite bed plugging problems due to suspended matter in the feed was experienced. An example of the composition of the secondary effluent before and after pretreatment (1) is given in Table 5.

TABLE 5

Composition of Richland Secondary Effluent
Before and After Lime Coagulation and Filtration

	Before	After
NH_4^+ as N, mg/l	11.5	10.4
Na^+ , mg/l	55	51
K^+ , mg/l	11	11
Mg^{+2} , mg/l	8.0	2.8
Ca^{+2} , mg/l	34	56
PO_4^{-3} as P, mg/l	7.5	1.6
COD	91	60
pH	7.2	6.5

Ammonia breakthrough curves for a clinoptilolite column receiving lime clarified Richland secondary effluent are shown in Figure 9. The curves illustrate the effect of Na^+ on the breakthrough capacity of the clinoptilolite. The presence of a significant amount of Na^+ on the exchange sites permits more rapid exchange for NH_4^+ than in the case where only Ca^{+2} is available for exchange. Self diffusion coefficients for Na^+ and Sr^{+2} (which is similar to Ca^{+2}) have been determined for Oregon clinoptilolite by Ames[29]. The diffusion coefficient for Na^+ was 8.43×10^{-8} cm^2/sec as compared to 1.0×10^{-8} cm^2/sec for Sr^{+2}.

*Nonionic polyacrylamide

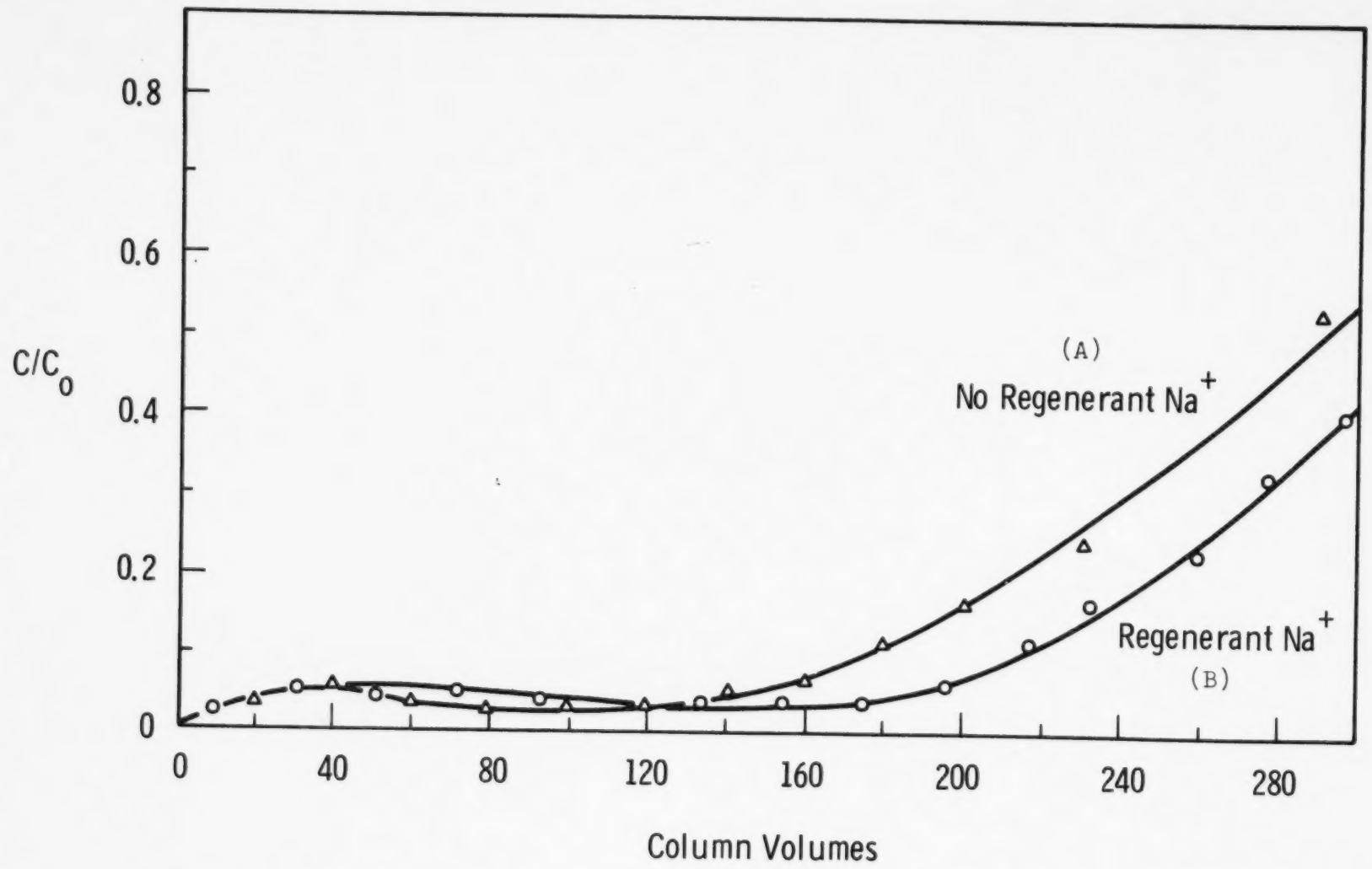

Figure 9. Effect of Na^+ in Regenerant on Subsequent Ammonia Breakthrough

Flow rate	20 cv/hr downflow.
Column dimensions	2" x 24".
Clinoptilolite grain size	20 x 50 mesh.
Temperature	26°C.
Feed	Limed coagulated and filtered Richland secondary effluent.
Previous regeneration	(A) 4.5g/l lime at 30 cv/hr upflow, (B) 4.5g/l lime, in 0.1N NaCl 30 cv/hr upflow.
Influent NH_4^+	(A) 14.0 mg/l as NH_3 - N (B) 13.0 mg/l as NH_3 - N.

The presence of Na^+ in the lime regenerant also sharpens the ammonia elution curve due to the more rapid exchange rate of Na^+ relative to Ca^{+2}. Ammonia elution curves are shown in Figure 10 for 3 different regenerant solutions containing lime. Curve 3 is similar to that of a saturated lime solution. Regeneration with a mixture of $CaCl_2$ and NaCl in a saturated lime solution, as shown by curve 2 in Figure 10, represents the most economical approach. The composition of this mixture is near that which results from continuous recycle of a regenerant solution ($0.1\underline{N}$ NaCl + $CaCl_2$) after air stripping to remove ammonia. Reuse of the regenerant after addition of make-up lime eliminates the problem of disposal of a wastewater concentrate to the environment[30]. A small amount of innocuous solid matter, largely calcium carbonate and magnesium hydroxide, is removed from the recycled regenerant for disposal.

The use of an alkaline material such as lime for regeneration may cause some leakage of ammonia during the initial part of the loading cycle. The leakage is caused by residual alkalinity (i.e. lime) which increases the pH of the column feed to the point where the ammonia is poorly ionized and therefore poorly adsorbed. Neutralization with CO_2 or HCl was investigated, but did not appear to be satisfactory due to the agglomeration of the clinoptilolite particles with $CaCO_3$ in the case of CO_2 or excessive consumption of acid in the case of HCl. The latter was caused by ion exchange with the clinoptilolite rather than neutralization. Thorough backwashing with ammonia free effluent from the loading cycle was found to be effective for removing the residual alkalinity.

The performance of two clinoptilolite columns in series is illustrated by the ammonia breakthrough curves in Figure 11. The first column had received 193 column volumes of effluent as a polishing column in a previous experiment. The second column in Figure 11 was placed in series with the first after 72 column volumes of feed had gone through the first column. The average ammonia removal was 98% in the product effluent from the columns. More than 99% removal of ammonia has been demonstrated in the laboratory with two columns in series.[31]

The second column in Figure 11 had previously been regenerated with 0.015 M NaOH. Sodium hydroxide may be desirable as a regenerant in some cases to avoid an increase in hardness of the effluent due to the use of lime. Regeneration with 0.015 M NaOH required about 35 column volumes. Higher concentrations

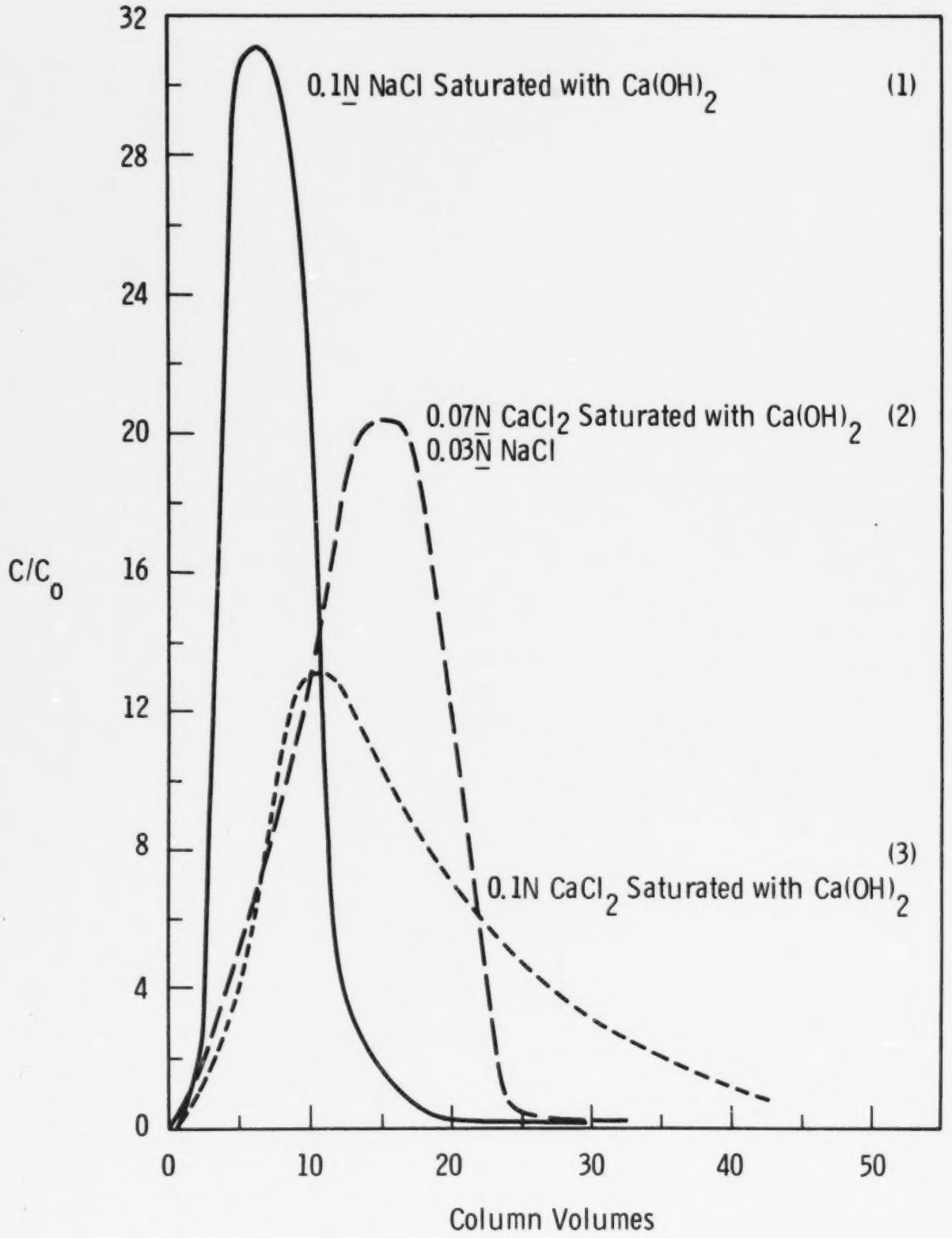

Figure 10. NH_4^+ Elution Curves for Three Regenerant Solutions

Flow rate	10 cv/hr upflow
Temperature	26°C

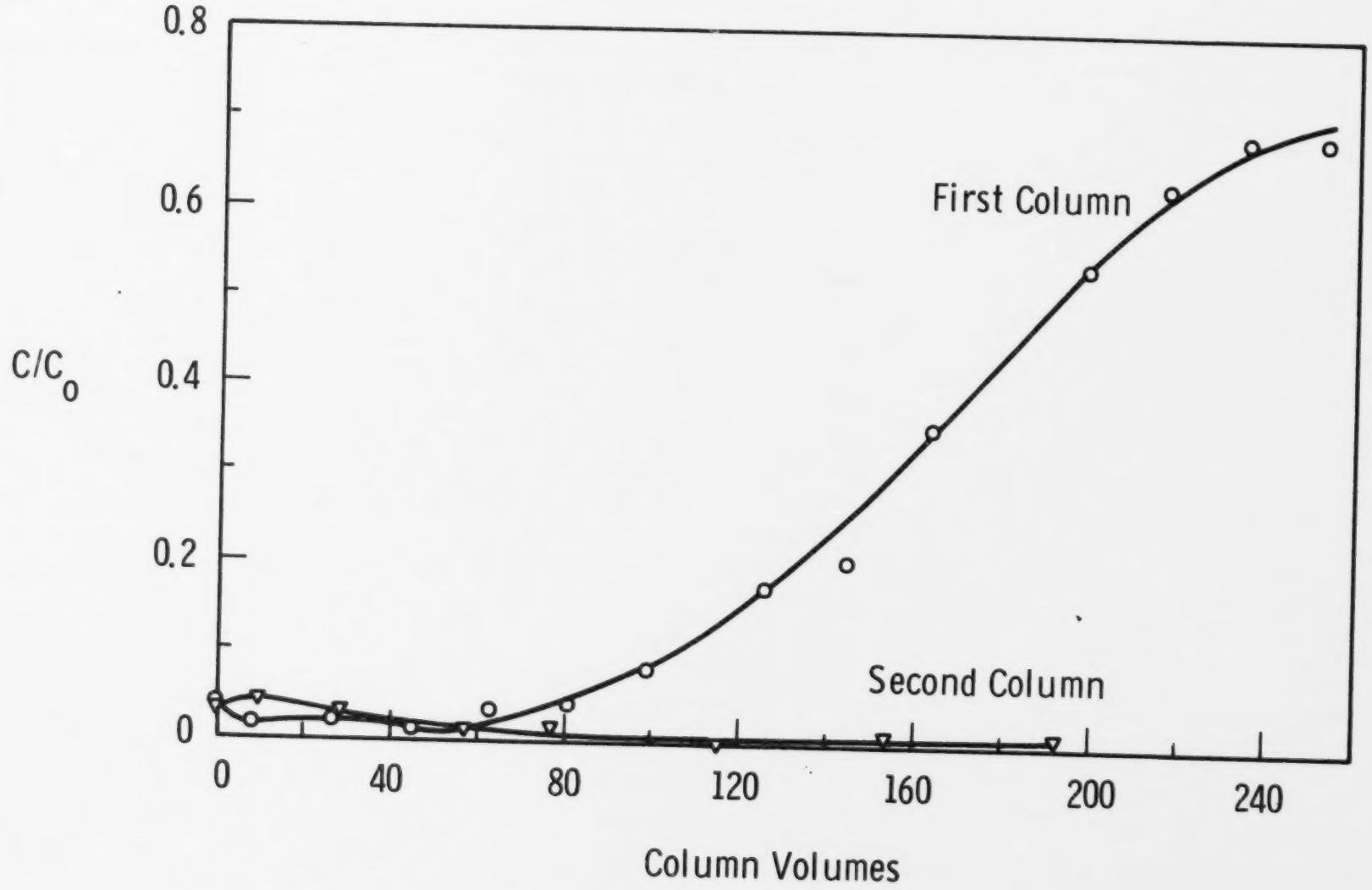

Figure 11. Ammonia Breakthrough for Two Clinoptilolite Columns in Series

Flow rate	20 cv/hr.
Column dimensions	2" x 24".
Clinoptilolite grain size	20 x 50 mesh.
Temperature	26°C.
Feed	Alum coagulated and filtered Richland Effluent NH_3 - N content 18.5 mg/l.
Previous regeneration	0.015N NaOH at 10 cv/hr, 40 cv total.

of NaOH may be used to reduce the volume of regenerant or the time required for regeneration. However, precipitation of $Ca(OH)_2$ or damage to the clinoptilolite probably will limit the strength of the caustic used. The chemical stability of clinoptilolite has been reported by Barrer, et al.[32]. A weight loss of 70% was determined for clinoptilolite crystals in contact with 20% NaOH for two days at room temperature. The relation between the amount of attack and concentration of NaOH was almost linear.

A 3 inch by 10 feet air stripping column packed with 1/2 inch Intalox^R* saddles was constructed in the laboratory to evaluate recycle of regenerant solutions. The spent regenerant solutions were fed to the top of the stripping column at 25 ml/min while air was introduced at the botton at 120 liters/min. This air/liquid ratio is equivalent to 640 ft^3/gal. The ammonia concentrations were reduced to less than 1 mg/l of NH_3 - N. The influent air and liquid temperatures were 25° ± 2°C. The stripper performance was evaluated at 3 different air/liquid ratios with a spent regenerant solution containing lime at pH 12 and 0.08 eq/l $CaCl_2$, 0.02 eq/l NaCl and 141 mg/l NH_3 - N. The ammonia removal was 29%, 86%, and 98.8% at 25°C for air/liquid ratios of 27, 87, and 111 ft^3/gal., respectively. Laboratory data on the effect of temperature at 24 ft^3 of air per gallon of spent regenerant showed an increase from 24% ammonia removal at 23°C to 78% at 50°C.

Recycled regenerant was used for 3 consecutive runs. The ammonia elution curve for the third run which is typical of the 2 preceding runs, is shown in Figure 12. The elution curve is relatively sharp and shows that regeneration is essentially complete at 20 column volumes. Laboratory studies indicate that as much as 14 mg/l NH_3 - N may be tolerated in a recycled regenerant without impairing the ammonia removal efficiency of a clinoptilolite column.

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* U. S. Stone Ware, Division of Norton Company, Akron, Ohio

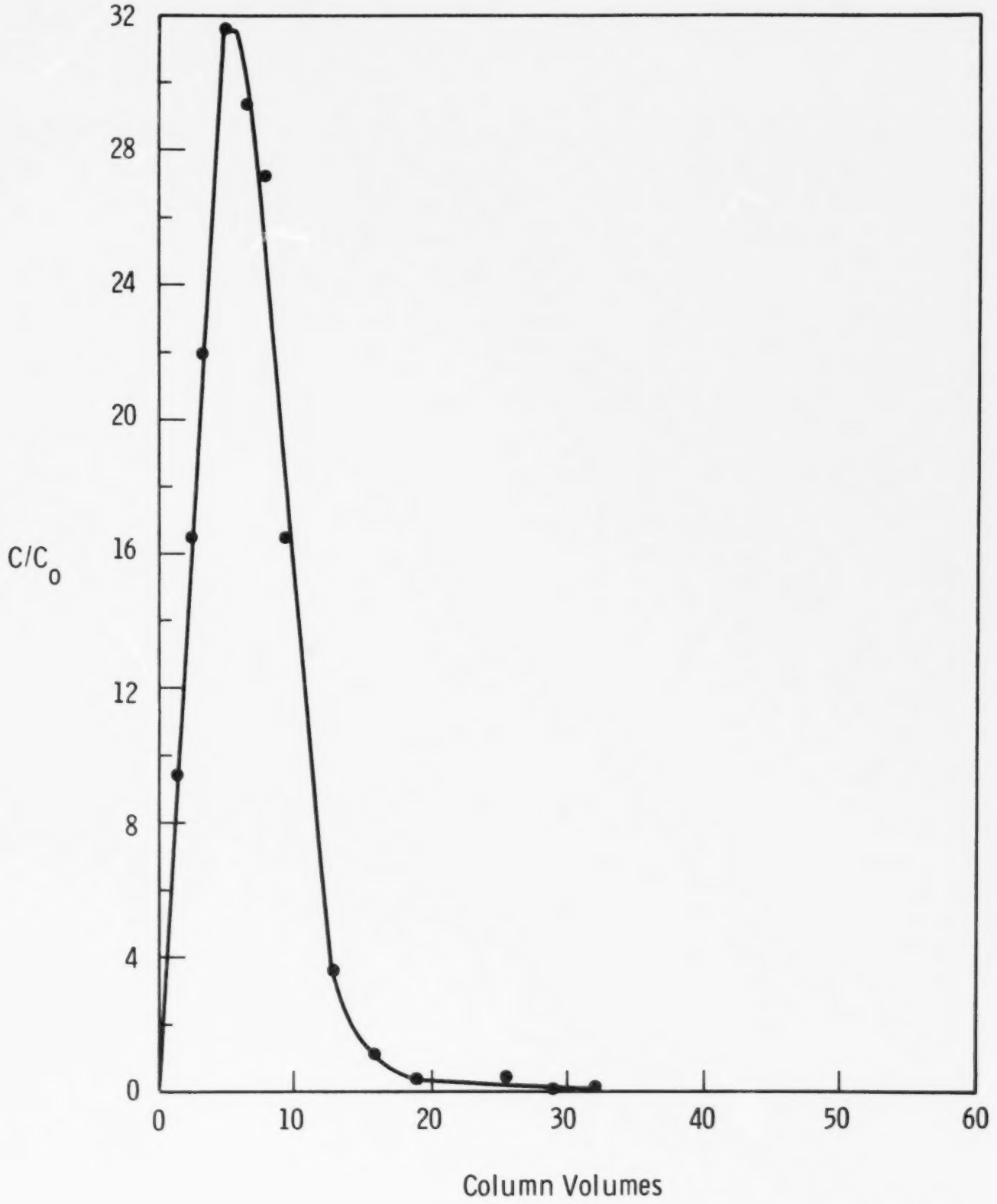

Figure 12. Ammonia Elution with Recycled Regenerant Saturated with Lime.

Flow rate . . . . . 10 cv/hr upflow.
Column dimensions . . . . . 2" x 24".
Clinoptilolite. . . . . 20 x 50 mesh.
Temperature . . . . . 26°C.

PILOT PLANT STUDIES

Demonstration Plant Description

The mobile demonstration plant houses three basic components; a Neptune MicroFloc, Inc.* 100,000 gpd model SWB tertiary filter unit, a complete ion exchange and regeneration system for ammonium ion removal, and a small wet laboratory for plant performance monitoring and control. **A photograph of the plant is shown in Figure 13.**

The tertiary filter unit serves to remove suspended matter from wastewater which might plug or foul the ion exchange beds. The unit contains equipment for chemical addition, flocculation, settling and filtration. Settling is accomplished in a compact chamber which contains many slightly inclined tube settlers. The overflow from the tube settlers is filtered with a course-to-fine mixed media filter bed and pumped to the backwash-filtered water storage vessel, which is a 3500 gallon portable swimming pool.

Since the ion exchange facility is the focal point of the investigation, it was designed to be versatile and flexible. This approach has aided greatly in achieving the experimental objectives as well as providing the capability for investigating unusual process flow configurations. The ion exchange facility includes three 750 gallon ion exchange vessels with removable top sections. These top sections extend through the roof of the forty foot trailer and are removed during transit. When the top sections are not used the vessels are converted to 500 gallon total volume capacity.

A 43 inch ID stripping tower also extends through the trailer roof during operation, and like the ion exchange vessels, its top is detachable for trailer transport. The stripping tower is packed with about 7 feet of 1 1/2" porcelain Intalox® saddles. The stripping tower liquid drains into a 200 gallon aqueous make-up tank with its own solids feeder and liquid mixer. Air for the stripping tower is supplied by a 10 Hp blower and is heated by a 60 kw heater bank.

A compact piping cross header is installed underneath the trailer frame, leaving about 18 inches clearance to the pavement of a flat road. The piping includes 36 electrically operated ball valves which allow the liquid flow in the ion exchange and regeneration cycles to be routed

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*Neptune MicroFloc, Inc., Corvallis, Oregon

Figure 13. Mobile Demonstration Plant for Ammonia Removal

between any conceivable origin and destination in the process. This is achieved by providing cross connections between four general purpose cross headers to any inlet or outlet point of the ion exchange vessels.

Six of the ball valves and one special purpose cross header serve special functions in the regeneration cycle. One of the general purpose headers is also diverted to serve the regeneration cycle when one of the ion exchange columns is being renewed. Figure 14 presents a schematic diagram of the ion exchange and ion exchange regeneration system. The figure also shows 1000 gallon regenerant storage which is provided by two 500 gallon polyethylene tanks.

Figure 15 (photograph) shows the demonstration plant control and process monitoring panel. Figure 14 is a diagram key to the control panel arrangement. At top left of the two-rack panel are the two temperature controllers for the stripper air and liquid heaters. These are fully transistorized Electro-General* controllers with full proportional action with reset and reset rate adjustable provisions. These controllers each modulate a Robicon** SCR solid state power controller - 60 kw for the air heater and 5 kw for the liquid heater.

Just below the temperature controllers are the switch and neon indicator light arrays for the thirty-six motor-operated ball valves in the trailer piping. Each valve may be controlled individually by one of the switches or in a predetermined way by a master transfer switch and a programmable 36 pole drum switch which simultaneously controls the other 35 valves as well. The individual valve switches are clustered in a 30 switch array and smaller cluster of six.

The main array is arranged to represent the valve connecting between the indicated header (column in the array) and ion exchange vessel top or bottom connection (row in the array). This arrangement is convenient for the experimental purposes where the desired mode of operating the process may be upflow or downflow, series or parallel, or any combination of these.

The lowest panel in the left hand rack contains the start-stop controls for the several pumps, the solids feeder, the blower, the two heaters, and the aqueous make-up tank water feed solenoid valve. Some of the equipment controls can be operated automatically, as well as manually, for unattended

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*Electro General Corporation; Hopkins, Minnesota

**Robicon Corporation; Pittsburg, Pennsylvania

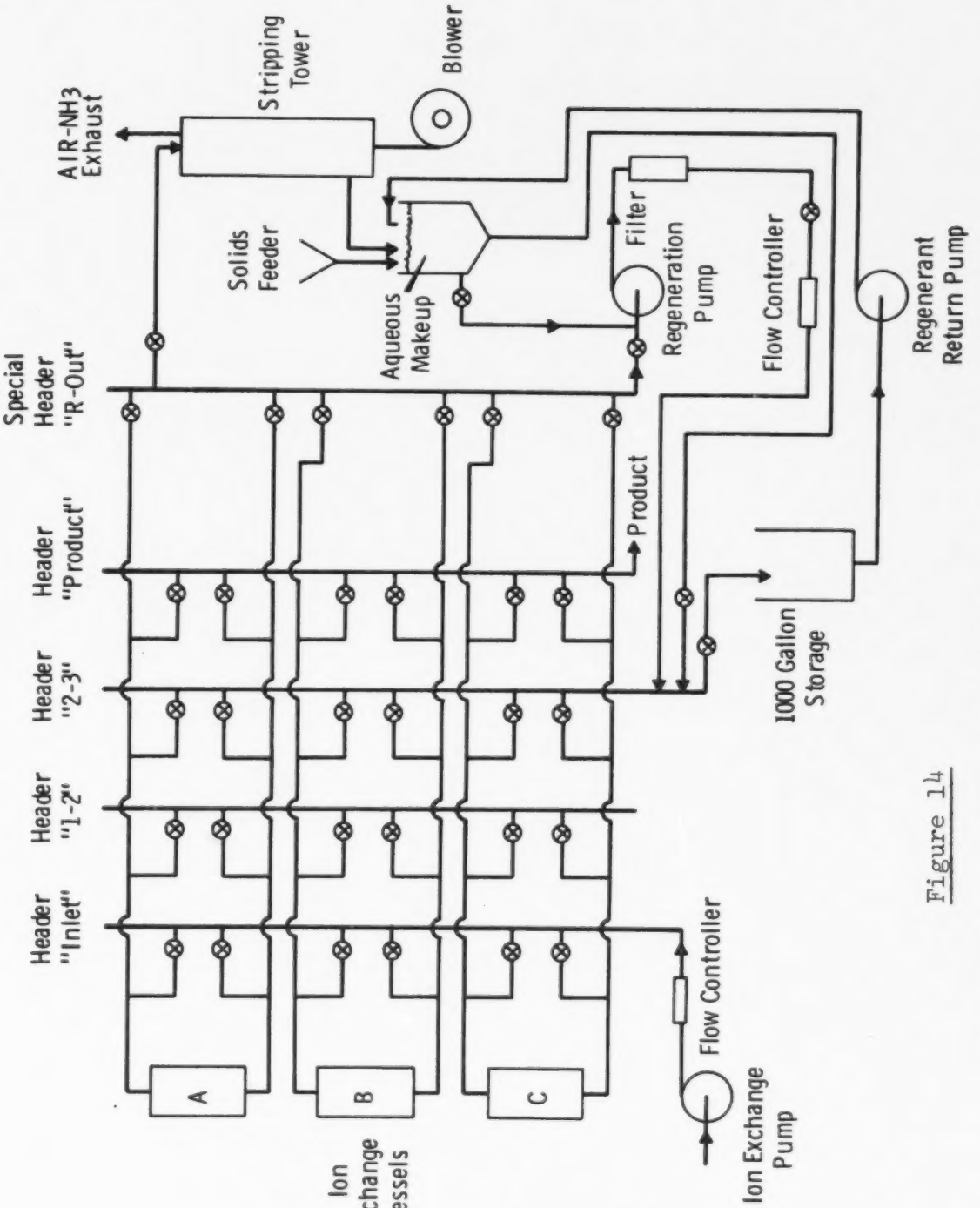

Figure 14

Ion Exchange Process Schematic

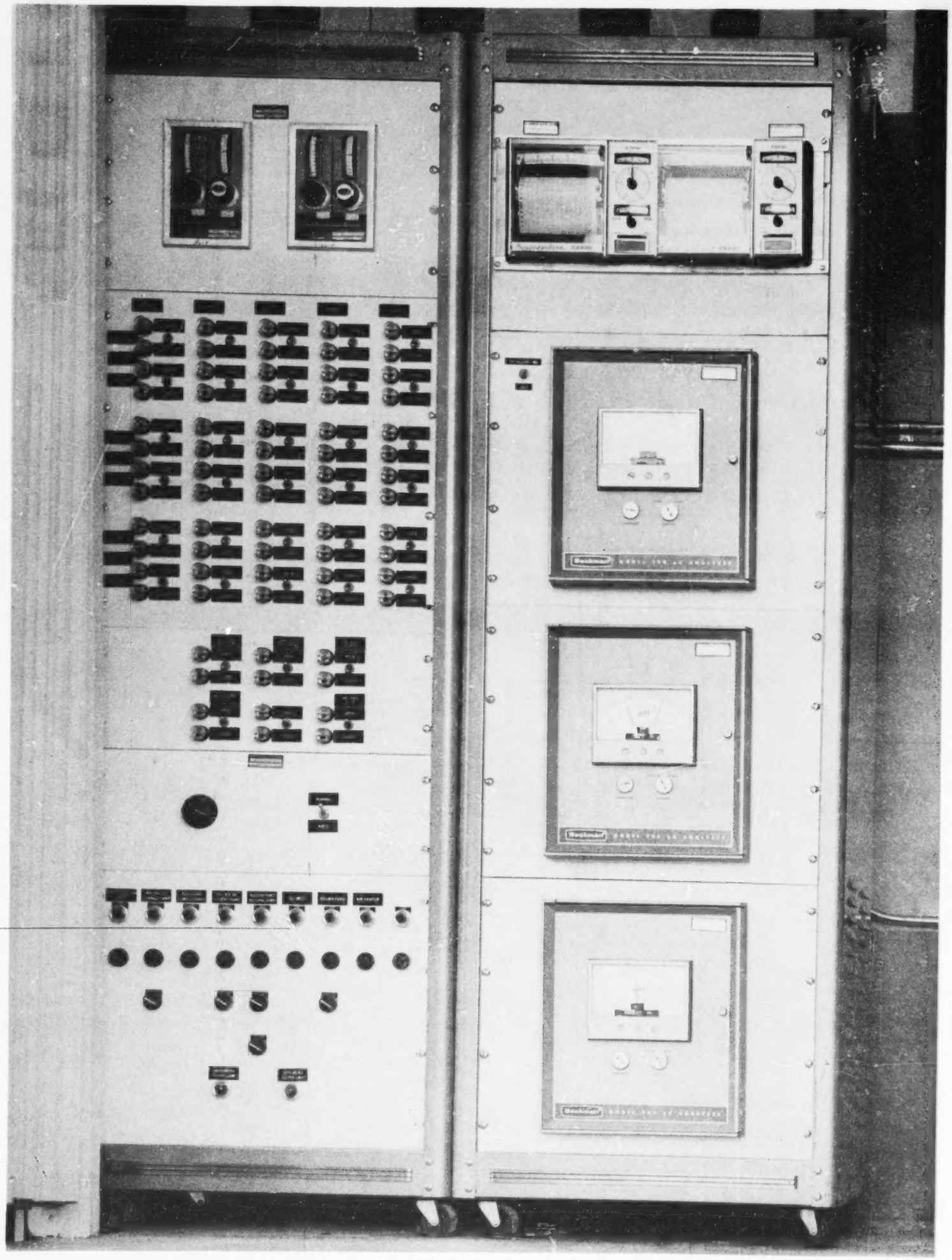

Figure 15. Demonstration Plant Control Panel.

operation. The ion exchange feed pump, for example, can be turned on and off automatically by the tertiary filter unit automatic controls, depending on the water level in the backwash storage pool. The solids feeder can be operated automatically when the regenerant pH drops below a preset value as measured by the regenerant pH monitor on the right hand panel.

Wastewater Pretreatment

This section will deal with the operation and performance of the Neptune MicroFloc wastewater pretreatment unit which was described in the previous section. Depending on the influent wastewater composition, pretreatment requirements may range from none or simple filtration up to complete treatment with the addition of powdered activated carbon, a chemical coagulant, and a polyelectrolyte followed by flocculation, settling and filtration.

Prior to operation of the filter unit, laboratory jar tests were conducted to establish required chemical concentrations for treatment of Richland secondary effluent. Based on the results of the jar tests and trial runs with the filter unit the chemical concentrations employed for the first two runs were as follows: 1) powdered activated carbon, 70 mg/l; 2) lime, 56 mg/l; 3) alum, 240 mg/l; and 4) polyelectrolyte, 2.5 mg/l. The lime was added to maintain the pH near 7. Table 6 contains analytical data for the pretreatment step for the first two runs.

COD reduction through the pretreatment system ranged from 34 to 61%. This relatively low COD removal is primarily a result of a very short contact time between the waste stream and the carbon prior to addition of the coagulating chemicals. However, the effluent from the system was sparkling clear from visual observation which is supported by the turbidity data reported. The effluent was also odorless. As would be expected with the alum concentration employed, the phosphate removal was highly efficient.

The first two runs were made at 70% of the design flow rate because of short filter run lengths, averaging about 2 hours. The short filter run time was caused by a poor hydraulic flow pattern to the tube settlers which was later corrected by a simple alteration in flow pattern from the flocculator.

Trailer test runs numbers 3 and 4 were conducted with only filtration of the secondary effluent as pretreatment. Turbidity of the secondary effluent was reduced from 10 JTU to approximately 6.3 JTU. Suspended solids were reduced from 28 to 23 mg/l.

TABLE 6 Analytical Data for Wastewater Pretreatment

	Secondary Effluent			Filter Effluent		
Sample	COD mg/l	Turbidity JTU	PO_4^{-3} mg/l P	COD mg/l	Turbidity JTU	PO_4^{-3} mg/l P
1	106		9.3	70		<0.16
2	115	11.2	8.5	45	0.63	<0.16
3	98	10.1	9.3	49	0.66	0.16
4		12.8	8.7		0.56	0.16
5	106	9.8		66	0.27	<0.16

Ion Exchange Processing

Studies were conducted with the mobile demonstration plant at the Richland wastewater treatment plant to evaluate the effectiveness of the selective ion exchange process for removing ammonia nitrogen from secondary effluent on a pilot scale. The mobile pilot plant was operated with 500 gallon clinoptilolite beds at a 70,000 gpd rate with clarified secondary effluent and at a 100,000 gpd rate with 330 gallon clinoptilolite beds and unclarified secondary effluent. The influent stream was pumped downflow through either a single clinoptilolite bed or two beds in series. Series operation permits greater utilization of the available ion exchange capacity since the service cycle of a single ion exchange bed is terminated at relatively low breakthrough whereas the first bed of a series can operate to a relatively high breakthrough. Freshly regenerated beds are placed at the end of the series to replace the loaded beds upon their removal from service.

The series mode of operation employing three ion exchange beds is described by the steps below starting with two beds in service while a third bed is being regenerated.

(1) When regeneration of the third bed is complete the regenerant is drained from the bed to the regenerant storage tanks.

(2) The freshly regenerated bed is rinsed with a small amount of water to recover any regenerant remaining in the bed and replace evaporated water.

(3) The first bed in series is removed from service when it approaches maximum loading.

(4) The freshly regenerated bed is placed in series upflow after the No. 2 column for a short period of time to remove residual alkalinity and small particulate matter (e.g., $CaCO_3$). Ammonia concentration in the effluent from the No. 2 column should be relatively low during the backwash period.

(5) When the backwash of the freshly regenerated column is complete it is placed in downflow service.

(6) The loaded column is drained in the meantime and a solution of NaCl and $CaCl_2$ (total 0.1 eq/l) containing lime is pumped through the bed upflow for regeneration.

(7) Spent regenerant is air stripped to remove ammonia, make-up lime is added, and the regenerant is recycled back through the column.

(8) Precipitated solids such as magnesium hydroxide and calcium carbonate settle out in the regenerant storage tanks and are periodically removed.

The first two ion exchange runs were conducted with clarified secondary effluent. Only a single bed was used in the first run since high head loss developed when an attempt was made to place a second bed in series with the first. The differential pressure across both beds reached the ion exchange vessel pressure test limit of 28 psig immediately upon placing the second bed in service. It was possible to place two in series during the second run, however, since the differential pressure remained just under 28 psig. No significant pressure increase was observed during either run.

All of the clinoptilolite beds underwent short regeneration cycles following the initial flushes made with clarified secondary effluent. The beds were backwashed with ammonia free effluent following regeneration. However, the backwash flow may have been insufficient to remove some of the small particulate matter. Addition of a storage tank for backwash water may be helpful, but it is doubtful whether the design flow rate of 100,000 gpd can be attained with two 500 gallon beds of 20 x 50 mesh clinoptilolite in series due to high pressure.

Breakthrough curves for the two clinoptilolite beds used in Run 2 are shown in Figure 16. The first bed was operated alone until ammonia breakthrough was detected at a throughput of 75,000 gallons. At this point a second bed was placed in series with the first. Average ammonia removal was 97% for the 154,000 gallons processed during the second run and the average effluent ammonia nitrogen concentration was 0.53 mg/l.

Lime solution containing 0.1 eq/l of NaCl + $CaCl_2$ was employed for regenerating the exhausted zeolite beds from the first two demonstration runs. A curve showing percent ammonia removal during regeneration and air stripping versus time is presented in Figure 17 for the column exhausted in Run 2. Loading data indicates that 17.5 lbs. of ammonia was adsorbed whereas the curve in Figure 17 indicates that regeneration was near completion at 15.2 lbs. of ammonia eluted. The difference is believed to be largely the result of fluctuation in the influent ammonia concentration which occurred outside of the scheduled sampling period.

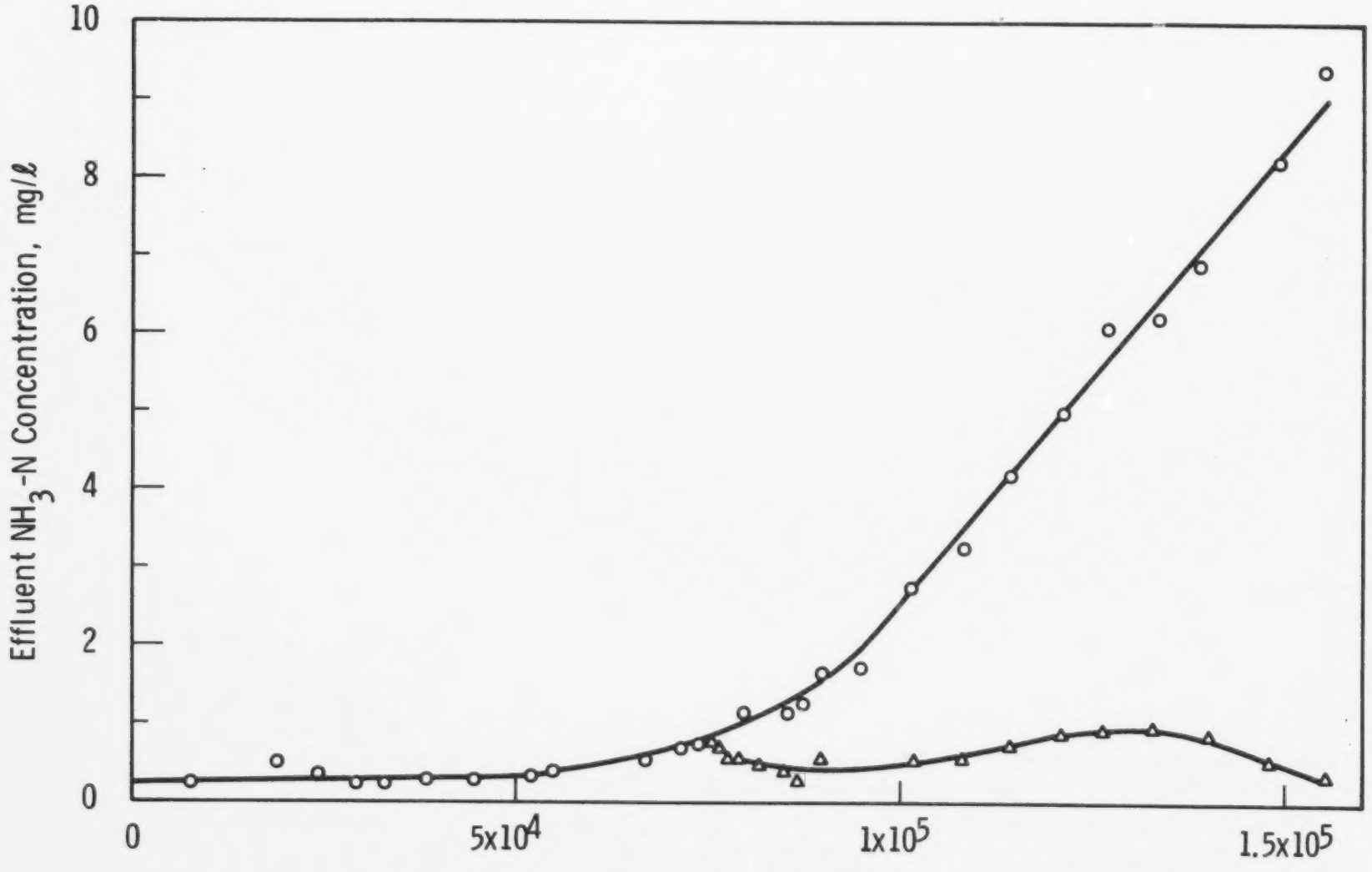

Figure 16. Ammonia breakthrough curves for 'C' and 'A' columns, Run No. 2.

Flow rate	50 gpm
Bed volume	500 gallons
Clinoptilolite grain size	20 x 50 mesh
Feed	Alum coagulated Richland secondary effluent
Influent NH_4^+	16.3 mg/l NH_3 - N average

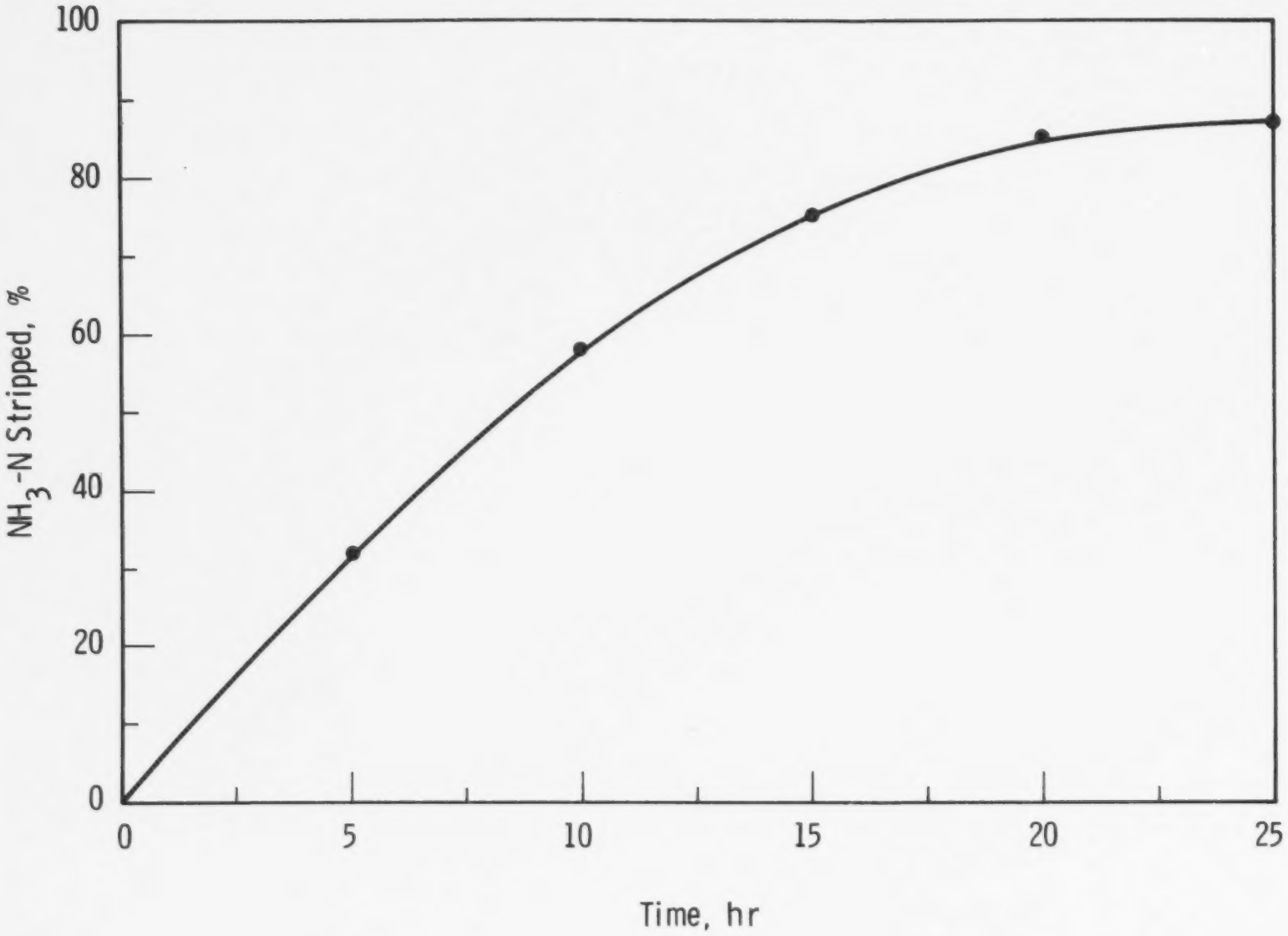

Figure 17. Run No. 2: Regeneration and Stripping Operation

The ion exchange beds were reduced in size from 500 to 330 gallons of clinoptilolite to evaluate their performance at the design flow rate of 70 gpm (100,000 gpd). The flow could not be achieved with two 500 gallon beds in series due to pressure difficulties. A bed volume of 330 gallons was selected since it was the maximum volume of zeolite which could be placed in the ion exchange vessels without the top section. One third of the available space in the vessels was thus alloted for bed expansion during backwashing. Chemical treatment of the secondary effluent was omitted in order to study the feasibility of this mode of operation. The multimedia filter was used essentially as a strainer to remove large particulate matter which might plug the ion exchange beds.

Ammonia breakthrough data with the filtered but unclarified secondary effluent showed an average ammonia nitrogen concentration of 1.1 mg/l for 138,250 gallons of product water. The ammonia removal averaged 93 percent. No increase in head loss occurred but the ammonia removal efficiency for the first column loaded was poor. The loss in efficiency is believed to have been caused by channeling in the zeolite bed.

Ammonia Stripping Operation

Ammonia is removed from the ion exchange regenerant at pH 10 -12 by countercurrent air stripping. The stripping tower used is 3 1/2 feet inside diameter by 11 feet 9 inches overall height. 6.6 feet of 1 1/2 inch Intalox® saddle packing provides a six theoretical transfer unit performance at the range of gas and liquid rates used in the stripping operation. Table 7 summarizes the specifications of the stripping tower and its packing. Figure 18, a cross section drawing of the tower, also shows the six inch thick de-entrainment mesh used at the tower top and the liquid separator at the bottom.

Air is supplied to the system by a 10 horsepower Sheldons* blower rated to deliver 1800 scfm at 20 inches water. The air passes from the blower through a 60 kva heater bank where its temperature may be increased to the 20-35°C range required at the tower air inlet to provide acceptable stripping performance.

The regenerant liquid enters the top of the stripping tower and sprays down onto the packing from a liquid distributor ring. The regenerant is scrubbed by the rising air as it passes through the packing, and then it is collected at the bottom of the tower and routed back to the aqueous

*Sheldons Manufacturing Corporation, Bensenville, Illinois

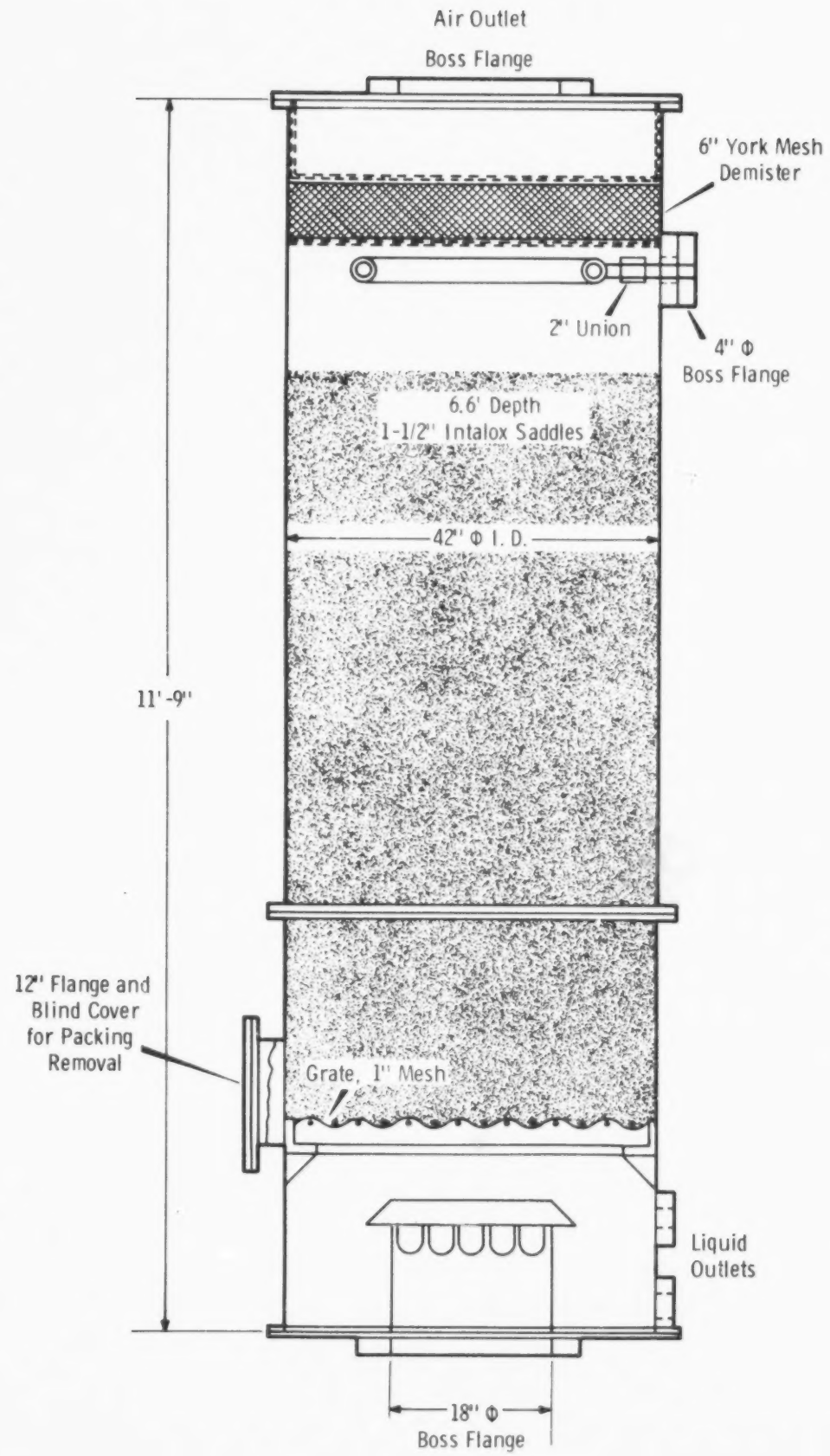

Figure 18. Cross Section Drawing of Stripping Tower

TABLE 7

Stripping Tower Specifications

Tower Cross Section	9.62 ft^2
Packing Height	6.6 ft.
Packing Material	1 1/2 inch Intalox^R saddles, Ceramic
Air Rate	4100 scfm (1880 lbs/ft^2-Hr.)
Liquid Rate at 18 gpm	936 lbs/ft^2-Hr
Air/Liquid Ratio	228 ft^3/gallon

make-up tank for chemical fortification and recycle to the ion exchange vessel being regenerated.

The performance of the stripping tower in Run 2 is presented in Figure 19. The stripping efficiency actually achieved is considerably lower than that reported elsewhere[33], observed in the laboratory studies, or predicted for the stripping tower operations. The most probable reason for the poor performance observed is liquid channeling preferentially down the tower side walls without being sufficiently contacted by the upflowing air stream. It is believed that the tower performance can be upgraded to its predicted efficiency by an improved liquid inlet distributor which should allow a complete regeneration-stripping time cycle of 18 hours or less.

It should be emphasized that the stripping tower was designed to fit the space limitations of the trailer van and as such the tower is relatively small. In order to provide adequate air-liquid contact an excessive amount of energy is required to drive the required volume of air through this small tower. In an actual plant process a relatively large stripping tower, such as a cooling tower[33] would be used to avoid a high pressure differential across the tower.

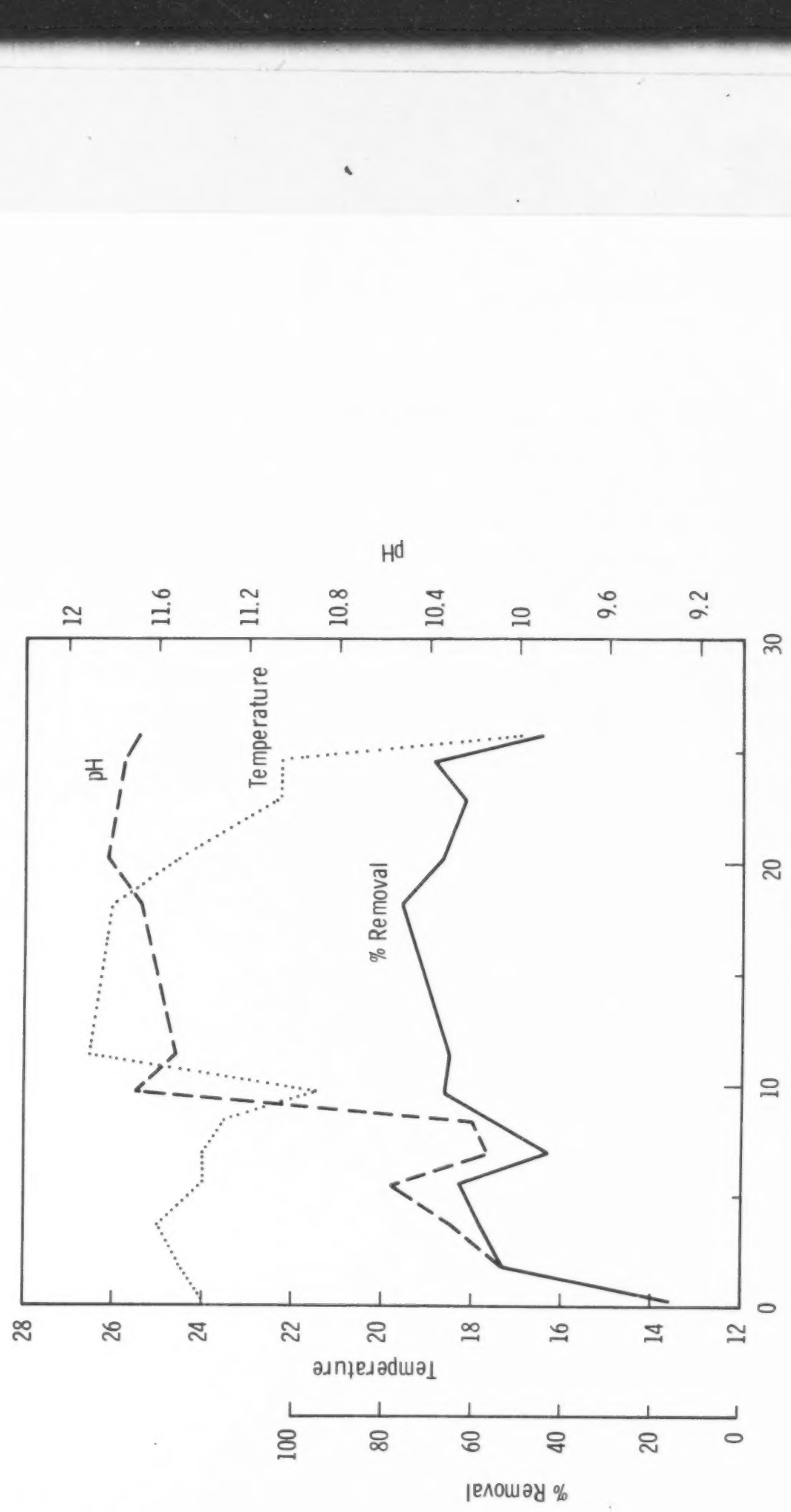

Figure 19. Run No. 2: Stripper Operation

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